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TECHNOLOGIES OF DELIVERY OR RECOVERY FOR THE REMEDIATION OF HAZARDOUS WASTE SITES

by

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16. ABSTRACT

Techniques to recover contaminants or deliver treating material at contaminated sites are described in the report. Few of the 17 described delivery or recovery techniques are in use today. New technologies, used in other industries such as petroleum extraction or mining, show promise for remediation of contaminated sites, but require investigation to affirmation of their suitability for in-situ remediation.

The following 17 technologies are described:

1. Colloidal gas aphrons
2. Hydraulic fracturing
3. Radial drilling
4. Ultrasonic methods
5. Kerfing
6. Electro-kinetics
7. Jet slurrying
8. CO_2 injection
9. Polymer injection
10. Vapor extraction
11. Steam stripping
12. Hot brine injection
13. In-situ combustion
14. Radio frequency heating
15. Cyclic pumping
16. Soil flushing
17. Ground freezing

Each description of a technology includes an explanation of the basic processes involved, the optimal site conditions for use, the current status of research, the personnel currently involved in research, and a list of references.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. the U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nuture lie. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinkng water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report describes 17 in situ delivery or recovery technologies that show promise for the remediation of contaminated ground or groundwater. The innovative technologies were identified during a literature review of topics related to hazardous waste site remediation, enhanced oil recovery, and solution mining. The information in this report is useful to those involved in the feasibility study and design of treatment alternatives for hazardous waste remediation sites.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

Remediating techniques that involve recovering contaminants or delivering treating material are particularly attractive because they can be less expensive and more permanent than either containment or excavation. A few delivery or recovery techniques are in use today, but on the horizon are new technologies that offer some exciting improvements in both the rate and the ultimate effectiveness of remediation.

The following report describes in situ delivery or recovery techniques that show promise for the remediation of contaminated ground or groundwater. Some of the technologies are currently being investigated for remedial actions, whereas others show promise but they have yet to be investigated for remedial purposes. Current investigations are funded chiefly by the USEPA or other government agencies. The promising technologies have been drawn from methods developed by the petroleum or solution mining industries. The following 17 technologies are described:

1. Colloidal gas aphrons
2. Hydraulic fracturing
3. Radial drilling
4. Ultrasonic methods
5. Kerfing
6. Electro-kinetics
7. Jet slurrying
8. CO_2 injection
9. Polymer injection
10. Vapor extraction
11. Steam stripping
12. Hot brine injection
13. In situ combustion
14. Radio frequency heating
15. Cyclic pumping
16. Soil flushing
17. Ground freezing

Each description of a technology includes an explanation of the basic processes involved, the optimal site conditions for use, the current status of research, the personnel currently involved in research, and a list of references.

Diagrams at the end of the report summarize the processes, required site conditions, and status of research into each technology. In addition, the diagrams facilitate comparison of what promises to be the next generation of techniques of delivery and recovery.

This report was submitted in fullfillment of Work Assignment 1-11 of contract 68-03-3379 by the University of Cincinnati under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from December 1987 to September 1988.

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SECTION 1

INTRODUCTION

This report reviews current research projects investigating innovative technologies that either recover contaminated groundwater or deliver remediating materials. Projects being investigated for the purpose of remediation are described, as are promising technologies from other industries that are untested in the field of remediation.

Basic definitions are needed to set the stage for the review of technologies that follow in section 2.

DEFINITIONS

Delivery and recovery technologies are processes that facilitate the transport of materials either into or out of the subsurface. Excluded are processes of *in situ* stabilization, such as mixing contaminated soils with cement or flyash, or *in situ* treatment, such as growing microorganisms that metabolize contaminants.

Delivery technologies, in general, involve transporting materials into the subsurface. Liquids are the principal phase in most delivery operations, although some of the new techniques allow either vapor or solid phases to be delivered as well.

Recovery technologies, in general, include any process to remove material from the subsurface. The principal recovery technologies used for remediation are associated with fluid flows driven by hydraulic gradients; also included however, are technologies driven by other types of processes, such as thermal methods, as well as processes to expedite recovery by employing chemical reactions that alter the behavior of contaminants.

The measure chosen to evaluate the effectiveness of a recovery technique is the average concentration of contaminants remaining in the subsurface at the end of the allowable life of the technique. This concentration bears directly on decisions of whether contamination has been sufficiently remediated at a particular site. For some technologies, data are available that permit quantitative measures of effectiveness, but for many other technologies, the required data are unavailable.

Site conditions are especially important because they highlight the extent to which a particular technology is applicable. Some technologies are valuable because they can be applied to a wide range of conditions; others are valuable because they can be applied to site conditions that are particularly difficult. *Site conditions* will be used to refer to those geological and hydrological characteristics of the subsurface, and those chemical characteristics of the contaminants affecting contaminant transport.

Of course, the utility of a particular technology depends on more than the simple measure of efficacy selected. For example, the cost and the time needed to employ the technology are central to possible practical applications. Cost should not be included in a definition of efficacy at this time because the applications are new and cost estimates are necessarily speculative. Because the time needed for many current technologies is excessive, many recovery technologies are being considered because they reduce the duration of remediation. Although time is not explicitly included in our definition of recovery efficacy, it is tacitly included by adopting a suitable allowable lifetime for the application.

THE NEED FOR FURTHER RESEARCH

Delivery and recovery techniques have been used for many years to remediate contaminated sites. So why are these techniques important as new research topics? Most currently-used techniques rely principally on pumping from recovery wells to remove contaminated groundwater followed by treatment and injection at delivery wells. Those pump and treat techniques reduce concentrations to acceptable levels for some contaminants and some site conditions. For many other conditions and contaminants, however, current methods cannot reduce concentrations to acceptable levels unless applied over an excessive amount of time.

Delivery of remediating materials, such as surfactants, oxidizing agents, or nutrients for bioremediation, is currently limited to injecting liquids through wells. Methods of delivering solid or vapor phases are currently unavailable in common practice although such methods would facilitate some remedial actions.

Current recovery methods rely primarily on inducing flow by creating gradients in total head; some techniques create gradients in gravity head, others rely on gradients in pressure head. In the following subsection, commonly used recovery methods are reviewed; their limitations highlight areas that need to be addressed by innovative technologies.

Gravity-Driven Methods

Delivery or recovery methods driven by gradients in gravity head are popular because they are simple and relatively inexpensive. Surface spraying, ponding, flooding, and ditch infiltration, for example, are used to deliver treatment solutions when contaminated soils are both near the ground surface and overlain by a permeable cover. Typically, these methods are limited to depths less than 16 feet and to soils whose hydraulic conductivities are in the range of 10^{-1} cm/sec to 10^{-3} cm/sec (EPA/540/2-86/002).

In the subsurface, gravity delivery methods are used when a contaminated zone is at a shallow depth or mantled by an impermeable cover. These methods include infiltration galleries and beds, which are excavations filled with porous material. The gravity-driven subsurface methods also require relatively large hydraulic conductivities, in the range of 10^{-2} cm/sec to 10^{-4} cm/sec (EPA/540/2-86/002).

Gradients in gravity head are also used to drive the recovery of contaminants. Perforated pipes or tile drains installed beneath, or trenches or open ditches cut adjacent to contaminated zones are simple recovery methods that are effective at some sites. Unfortunately, the use of gravity-driven recovery techniques is limited by some narrow restrictions, such as a maximum practical depth of 16 feet and a lower limit of 10^{-3} cm/sec of the hydraulic conductivity of the contaminated material (EPA/540/2-86/002).

Low-permeability layers are required beneath some applications of gravity-driven recovery methods to inhibit migration. Such layers are typically absent and must be emplaced artifically if the gravity driven method is used.

Pressure-Driven Methods

Methods driven by pressure involve forcing a fluid into a contaminated zone by injection into wells. The wells can be open-ended or slotted, and they are either driven into the ground or emplaced in borings.

Delivery techniques that are driven by gradients in pressure head, so-called *forced* delivery, involve injecting materials using pumps. Forced delivery methods are more effective than gravity methods in materials of low permeability, and currently available methods of forced delivery are most effective where hydraulic conductivities exceed 10^{-4} cm/sec (EPA/540/2-86/002).

Forced recovery techniques require pumps to reduce pressure heads below ambient conditions so the treatment fluid or contaminated fluid can be removed from pipes or wells. The two basic types of forced recovery systems are wellpoint systems using suction pumps at the ground surface and deep-well systems using submersible pumps placed at the bottom of recovery wells. Wellpoint systems are used when the water table is near the surface (less than 26 feet, the limit of suction); whereas deep-well systems are used at depths exceeding the limit of suction (EPA/540/2-86/002).

Limitations of Current Methods

Currently available methods of delivery and recovery have many shortcomings. The most widespread limitation is a practical exclusion from applications in tight formations where hydraulic conductivities are less than 10^{-4} cm/sec.

Contaminants with low water solubilities or those that are readily adsorbed to soil can have extremely slow rates of recovery. Another recently recognized restriction to recovery rate of many natural systems is the presence of preferred pathways of high conductivity separated by matrix blocks of low permeability. Recovery rates from such systems are limited by rates of diffusion through matrix blocks to the preferred pathways.

Recovery from unsaturated zones remains difficult. Low hydraulic conductivities and local stagnant zones in unsaturated media inhibit rates and effectiveness of recovery. Furthermore, some current recovery methods applied to the unsaturated zone require an underlying impermeable barrier that precludes their use at some sites.

INNOVATIVE TECHNOLOGIES

An innovative technology is a process that offers some improvement when compared with existing methods. For hazardous waste remediation, improvements either in the rate of recovery or in the amount of contaminants remaining in the subsurface are considered valuable.

Improvements in delivery would occur if either a method of delivering an increased volume of a liquid phase, or a method of delivering vapor or solid phases was developed. For example, the injection of a colloidal suspension of either minute solid particles or micron-sized vapor bubbles is one innovative delivery technology that is being investigated.

The scope of innovative processes for recovering contaminants is truly remarkable. Some processes include methods of increasing yields of recovery wells, either by creating zones of high permeability to increase drainage, inducing electrical fields that drive water flow, or cycling the rate of pumping. Others improve recovery by driving contaminating liquids into a vapor phase or by cutting a subsurface excavation to physically remove both contaminants and the soil or rock matrix.

Chemical methods can facilitate recovery by either increasing contaminant solubility in water or reducing contaminant adsorption to the surfaces of mineral grains. Thermal methods in which subsurface temperatures are increased improve recovery either by volatilizing or reducing the viscosity of contaminants. Other methods reduce soil temperature to the freezing point of water and induce migration of contaminants by processes associated with the phase change from liquid water to ice.

IDENTIFYING INNOVATIVE TECHNOLOGIES

The innovative technologies described in section 2 were identified during a literature review of topics related to groundwater recovery, enhanced petroleum recovery, and mining. Some of the technologies are currently being investigated as possible remediation methods, whereas others, principally the ones from the petroleum and mining industries, have yet to be investigated. They may, however, offer potential as remediation methods.

The information describing delivery and recovery technologies came from literature surveys and expert interviews. The literature surveys were conducted by initially searching appropriate computer databases to identify pertinent articles. Articles were obtained from local libraries, through interlibrary loans, and directly from the author or publisher. Published descriptions were insufficient to adequately describe a few of the technologies, so interviews were conducted with researchers or developers.

The innovative methods of delivery or recovery identified during our investigation are summarized in following list.

	Delivery Technology	Recovery Technology
1. Colloidal gas aphrons	Y	N
2. Hydraulic fracturing	Y	Y
3. Radial drilling	Y	Y
4. Ultrasonic methods	N	Y
5. Kerfing	Y	Y
6. Electro-kinetics	Y	Y
7. Jet slurrying	N	Y
8. CO_2 injection	N	Y
9. Polymer injection	N	Y
10. Vapor extraction	N	Y
11. Steam stripping	N	Y
12. Hot brine injection	N	Y
13. In situ combustion	N	Y
14. Radio frequency heating	N	Y
15. Cyclic pumping	Y	Y
16. Soil flushing	N	Y
17. Ground freezing	N	Y

SECTION 2

REVIEW OF INNOVATIVE TECHNOLOGIES OF DELIVERY OR RECOVERY

Some technologies of delivery or recovery identified and described here are fully developed in fields other than remediation; a large body of information is available describing them. Other technologies are in their infancy, and only preliminary data are available. To avoid favoring the better-developed technologies a consistent format is used to describe all technologies:

Description: A review of the basic processes and methods used by the technology.

Documented Applications and Limitations: An outline of the site conditions required for the efficient application of the technology. Site conditions are related to geology and hydrology of the site, and the chemistry of contaminating species. *Documented* uses of the technology provide an assessment of the performance of the technology at the bench, pilot or field scale.

Status: A report of where the technology is being investigated, and the scope and progress of research. The four possible states of development for each technology are based on developmental states used elsewhere by the EPA:

1. Available: Technology is fully proven and available for use.

2. Developed: Technology has passed bench and pilot-scale testing, but lacks thorough field testing.

3. Emerging: Research in progress, bench and pilot-scale testing incomplete.

4. Conceptual: Technology appears to be applicable to remediation, but research has yet to be initiated.

Bibliography: References cited in the text.

The following sections contain reviews of the 17 innovative technologies identified during this investigation.

COLLOIDAL GAS APHRONS

The use of gas aphrons, which are microscopic bubbles of vapor, has been suggested as a technique to enhance the in situ aerobic biodegradation of dissolved and dispersed organic contaminants. This suggestion is based on laboratory experiments showing that aphrons deliver a much greater concentration of gas when compared with methods that deliver gases dissolved in water (Michelsen and others, 1984).

Description

Colloidal gas aphrons (CGA) are microdispersions of gas in water. Typically, a CGA dispersion is 60 to 70 volume percent gas occurring in the form of minute bubbles or aphrons. The gas remains in the vapor phase, and the amount that can be delivered is independent of solubility.

Aphrons have a structure similar to a free floating soap bubble, but they approach colloidal in size (25 to 50 microns in diameter) and demonstrate colloidal properties (Auten and Sebba, 1984). At concentrations less than 65 volume percent, the viscosity and flow characteristics of a CGA dispersion in water are similar to those of pure water. Thus, CGA dispersions can be pumped through pipes, sand packs, or pores in soil or rock. The aphrons do not coalesce when they collide, and they tend to remain stable and suspended for long periods of time at temperatures up to 35° or 40°C (Michelsen and others, 1985).

Any gas of limited solubility and almost any water soluble surfactant can be used to produce a CGA dispersion (Michelsen and others, 1985), although most of the proposed applications involve the formation of air-filled aphrons in water. Early CGA's were created by passing a dilute surfactant solution at high velocity past a narrow gas entry port situated at a venturi throat. Air is sucked into the venturi at the throat and sheared off by solution passage when the velocity of the solution flowing through the venturi exceeds a critical velocity. The suction of the air causes colloidal-sized bubbles to be introduced into the solution. More recently, CGA's have been generated using a spinning disk in a baffled chamber (Michelsen and others, 1987).

Currently, each of the two proposed methods for in situ delivery of CGA's depends on the type of contaminated media in which it will be used. In saturated impoundment sediments, injection plows are probably most suitable (Michelsen and others, 1984). In saturated subsoils and perhaps in the capillary zone above the saturated region, CGA's can be delivered through injection wells (Michelsen and others, 1984).

The potential application of CGA's for hazardous waste remediation centers on using the microscopic bubbles as an oxygen source for in situ bioreclamation (Michelsen and others, 1986). The contaminated medium retains CGA's for long periods of time whereas air directly injected moves rapidly toward the unsaturated zone and allows very little air retention in the medium (Michelsen and others, 1986).

Documented Applications and Limitations

Laboratory experiments indicate that the use of CGA's may be limited to permeable sands and sandy soils. For colloidal gas aphrons to be an effective oxygen source, the contaminants must be located in the saturated zone or at the saturated/unsaturated interface (Michelsen and others, 1986).

Bench-scale bioreclamation studies showed that CGA's (along with microbes and nutrients) injected into a saturated anaerobic sand matrix contaminated with phenol effectively degraded 60 percent of the phenol in 24 hours (Michelsen and others, 1986). In laboratory bioreclamation testing, the effect of aphrons containing oxygen was compared with aphrons containing air. CGA's containing oxygen were more effective; 90 percent of hexadecane contaminating a model aquifer was degraded as compared with 70 percent for the CGA's containing air (Michelsen and others, 1986).

The migration of aphrons appears to be limited to a few feet from point of injection, apparently because CGA's may locally block or plug pores in soil. As a result, CGA use may be best suited to creating a reactive barrier through which contaminated groundwater would flow (Michelsen and others, 1987).

Status

Colloidal gas aphrons is an *emerging* technology used for delivery in remedial applications. CGA technology is being investigated at the bench- and pilot-scale levels at Virginia Polytechnic Institute and State University (V.P.I.) in Blacksburg, Virginia. Principal investigators include Donald Michelsen, David Wallis, Felix Sebba, and Steven Lavinder.

Colloidal gas aphrons is a developed technology for general applications. CGA technology has been tested at the bench- and pilot-scale levels for application to the floatation of ultrafine particles during mineral processing. This research is being conducted at V.P.I. Principal investigators include Felix Sebba and W. L. Auten.

Sources

Data on CGA technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Donald Michelsen of V.P.I. and Ronald Lewis, USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of CGA research.

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HYDRAULIC FRACTURING

Hydraulic fracturing is a technology that could be used to increase the rates of either delivery or recovery. It is used extensively within the petroleum industry both to stimulate the recovery of hydrocarbons from low permeability reservoirs, and to enhance the delivery of fluids used to displace petroleum in sweeping operations.

Description

Hydraulic fracturing is a process of cracking rock in the neighborhood of a borehole (Fig. 1). The cracks are formed by injecting a fluid, usually water, at pressures exceeding the confining stress at the bottom of the borehole. The fluid typically opens a single fracture that propagates away from the borehole. Some hydraulic fractures are horizontal, others are vertical. Sand pumped into the fracture at the time of its creation holds the fracture open forming a high-permeability channelway suitable for either the delivery or recovery of fluids (Fig. 1; Murdoch and others, 1987 and references cited therein).

Preliminary investigations, which consist of theoretical calculations, analogies to applications reported by the energy industry and small-scale field testing, suggest that hydraulic fractures can be created in the types of soil and rock common at many hazardous waste sites. The orientation of the fractures is expected to be either horizontal in rock and over-consolidated soil or vertical in normally consolidated soil (Murdoch and others, 1987). Lengths of hydraulic fractures are expected to be similar to their depths of origin; widths are expected to range from several mm to several cm. Some horizontal fractures lift their overburden and they could be one or more dm thick (Murdoch and others, 1987).

Possible applications of hydraulic fracturing include increasing the efficiency of pump and treat systems, stimulating the extraction of vapor phases from tight soils, or forming horizontal sheet-like drains to capture the permeant in a leaching operation (Murdoch and others, 1987).

Documented Applications and Limitations

Hydraulic fractures have been formed in many geologic materials, ranging from granite to poorly consolidated sediments. Workers in geotechnical fields have described hydraulic fractures in various soils (e.g. examples cited in Murdoch and others, 1987), and recent bench-scale experiments conducted at the Center Hill Research Facility suggest that hydraulic fractures can form and propagate in soft clay soil.

A recent field test has established that hydraulic fractures can be formed in unconsolidated materials at shallow depths. Shallowly dipping fractures were created at wells drilled to depths of 2 meters in glacial till. The fractures were larger than expected; maximum lenghts of the fractures were one to seven times the depth of fracture initiation.

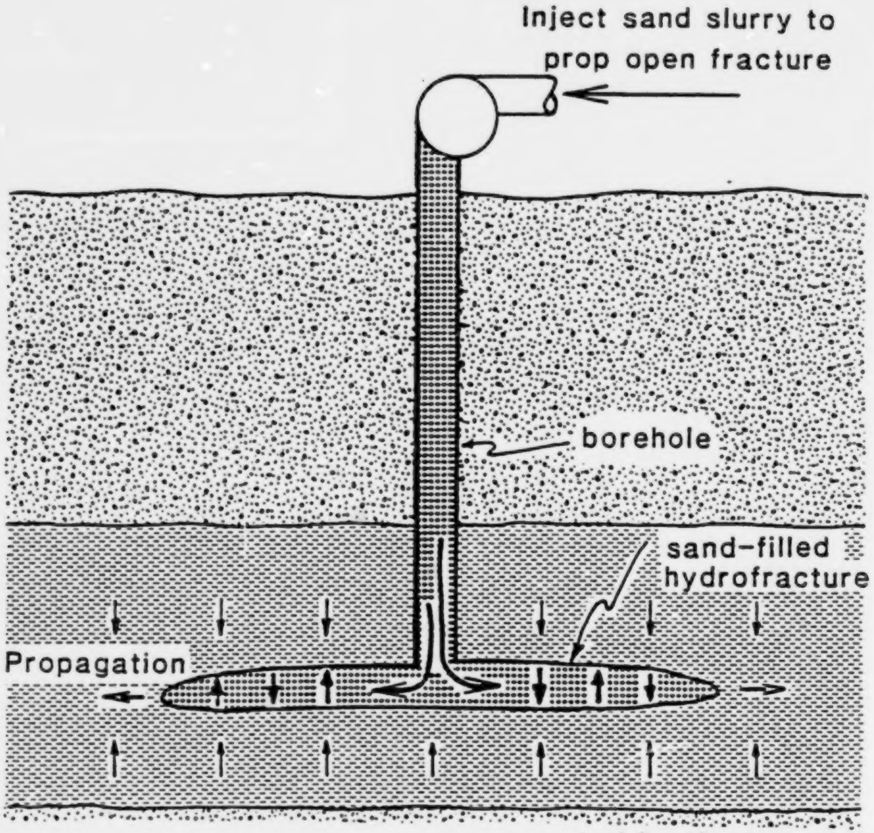
Inject sand slurry to prop open fracture
borehole
sand-filled hydrofracture
Propagation

Figure 1. Formation of a hydraulic fracture. Fluid is injected into the subsurface at pressures exceeding the confining stresses at the bottom of the borehole and creates a single vertical or horizontal fracture that propagates away from the borehole. Sand is pumped into the fracture at the time of its creation to hold the fracture open, forming a high-permeability channelway (after Murdoch and others, 1987).

The performance of hydraulic fractures in delivery and recovery operations involving groundwater remediation has never been described, but it can be estimated based on petroleum industry results and on theoretical analysis. When compared with the rate before fracturing, hydraulic fractures in oil wells routinely increases the rate at which a well will yield oil by a factor between two to ten. In some cases, the rate of increase is several orders of magnitude (Murdoch and others, 1987).

The volume of groundwater recovered from a hydraulically fractured well can be estimated theoretically as a function of time. Of course, the recovered volume depends on a great many factors, not the least of which are the length, width, and conductivities of the fracture and the enveloping formation (Fig. 2). Applying the theory to expected values of those variables indicates that the volume of water recovered from a well intersecting a hydraulic fracture could be an order of magnitude or more larger than the volume recovered from an unfractured well (Murdoch and others, 1987).

Status

Hydraulic fracturing is an *emerging* technology used for both delivery and recovery in remedial applications. Hydraulic fracturing technology is being investigated at the bench- and pilot-scale levels at the Center Hill Facility, University of Cincinnati, Cincinnati, Ohio. The principal investigator is Larry Murdoch.

Hydraulic fracturing is an *available* technology for general applications. It is fully proven and in routine use for enhanced oil production. Numerous oil field service companies including the Halliburton Services Company or Dowell Schlumberger can provide hydraulic fracturing.

Sources

Data on hydraulic fracturing technology were obtained primarily from the reference listed in the following bibliography. Additional information was acquired from Larry Murdoch, who is currently researching hydraulic fracturing; and Douglas Keller, USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of hydraulic fracturing research.

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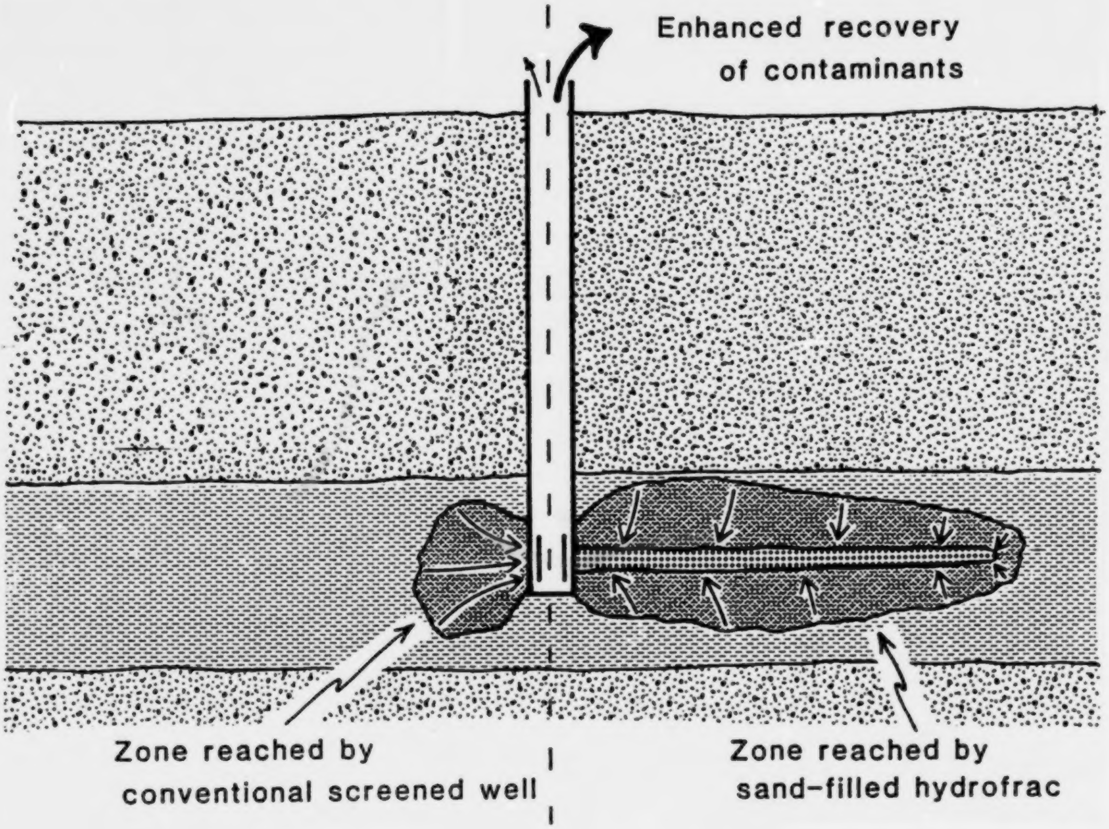
Enhanced recovery of contaminants
Zone reached by conventional screened well
Zone reached by sand-filled hydrofrac

Figure 2. The zone accessed by a sand-filled fracture compared with that of a conventional screened well (after Murdoch and others, 1987).

RADIAL WELL DRILLING

Horizontal wells drilled radially outward from a central borehole can be used to enhance access to a contaminated formation or aquifer. They can be used for either delivery or recovery. Many radial wells can be placed at the same level or on multiple levels in the same borehole. The potential applications of radial wells include groundwater control and in situ treatment. Horizontal wells have the ability to intersect fracture zones that are perpendicular to the ground surface or to intercept groundwater moving horizontally, allowing contaminant plumes to be entered laterally rather than vertically (Dickinson and others, 1986b).

Description

Early applications of horizontal wells employed a large diameter caisson from which horizontal wells were drilled radially outward (Bouwer, 1978). Because a worker typically was required to descend into the caisson to drill the horizontal well, early applications of this technique were very limited.

More recently, researchers in the petroleum industry (Petrolphysics Ltd. and Bechtel Investments, Inc.) have developed a method of drilling horizontal wells that radiate from a central well 4.5 inches in diameter or larger. With this new method, horizontal radial wells can be drilled at virtually any depth.

This new method of making horizontal wells has two key elements: a jet nozzle fixed to 1.25-inch diameter tubing, which is used to create the horizontal well; and a whipstock, which is placed at the bottom of the vertical borehole to redirect the nozzle and tubing horizontally into the formation (Fig. 3).

The horizontal radial is cut by high velocity water pumped out of a conical jet nozzle (Fig. 3). The nozzle is fed from the surface through steel tubing and cuts a borehole with a diameter several times larger than the tubing. An assembly of vanes placed upstream of the nozzle imparts a rotational component of flow to the fluid that exits the nozzle orifice (Dickinson and Dickinson, 1987d).

The high-velocity nozzle is used not only to cut the borehole, but static pressure on the inside of the nozzle results in a force that pulls the nozzle and attached tubing down the drill stem, through the whipstock and into the formation (Dickinson and Dickinson, 1985). This force also tends to keep the radial well progressing in a straight line.

The other key element, the whipstock, is placed and erected in a 24-inch diameter, underreamed cavity. The whipstock is composed of a series of slides and wheels that redirects the tubing from a vertical orientation in the central well through a 90° bend to a horizontal orientation. The forced redirection of the tubing by the whipstock is accomplished in only a 9-inch to 12-inch bend radius (Fig. 3; Dickinson and others, 1987b).

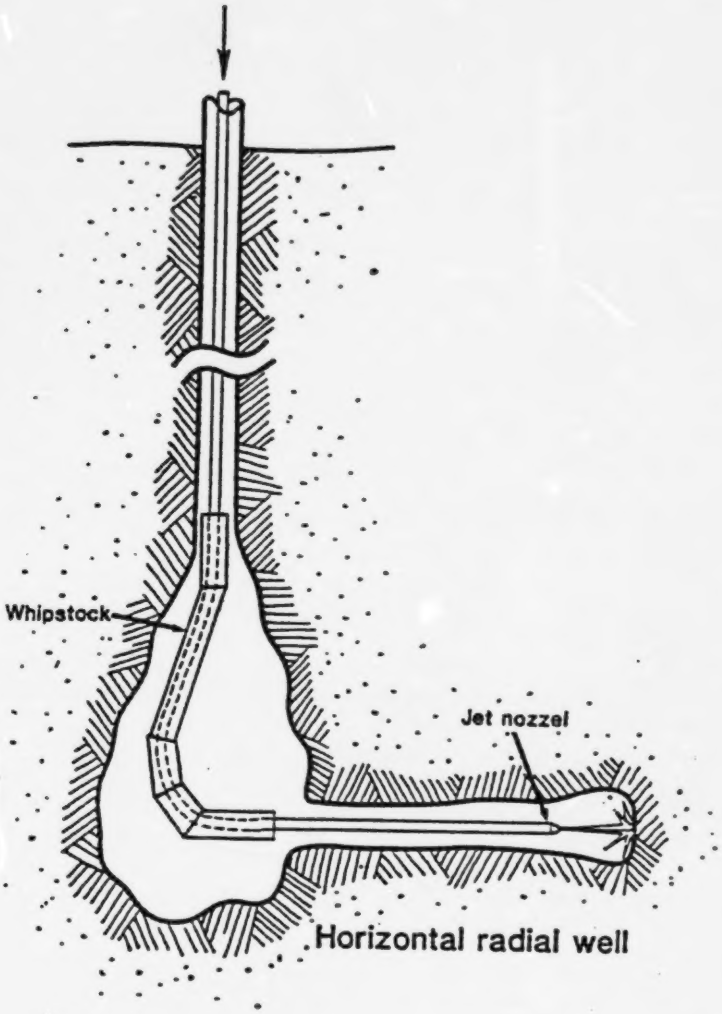

Figure 3. Creating horizontal wells. A whipstock redirects the tubing from a vertical orientation to a horizontal orientation. Static pressure within the nozzle exerts a force which pulls the nozzle and attached tubing down the drill stem, through the whipstock and into the formation. A high-velocity jet cuts a horizontal borehole with a diameter several times greater than the steel tubing (after Dickinson and others, 1986a).

A wireline logging system has been developed to precisely locate the radial well in space. The narrow tool is run through the 1.25-inch tubing. The wireline tool logs horizontal and vertical location and records the length of the horizontal radial well (Dickinson and Dickinson, 1985).

Completion techniques have been developed to electrochemically perforate and cutoff the tubing within the radial, place a slotted liner within the perforated tube, and gravel pack the radial. The gravel packing is done in two lifts: in the first lift, gravel is pumped out from the end of the 1.25-inch tube and forced towards the borehole; in the second lift, gravel is forced from the borehole into the radial (Dickinson and others, 1987a).

Documented Applications and Limitations

Experimental and commercial radials have been placed in both consolidated rock and unconsolidated material. The rate of placement in rock is much less than in unconsolidated material. In unconsolidated formations, typical drilling rates range from 5 to 120 ft/min (Dickinson and others, 1986b). In very hard, homogeneous basalt, the rates range from 0.10 to 0.50 ft/min (Dickinson and others, 1987c).

Horizontal radials can be placed in both saturated and unsaturated conditions and would assist in remediation by increasing the volume of that medium serviced by each vertical well (Dickinson and others, 1987b).

Over 500 horizontal radials, totaling 27,000 feet in length have been placed at depths ranging from a few feet to almost 7,000 feet and in formations ranging from unconsolidated sand in California to chalk in Texas and salt in Canada (Dickinson and others, 1987b). Of these 500 horizontal radials, over 100 have been placed in a single test well (Dickinson and others, 1986b).

Status

Radial well drilling is an *emerging* technology used for both delivery and recovery in remedial applications. It is being investigated at the bench- and pilot-scale levels by Petrolphysics, Ltd. in San Francisco, California. Principal investigators include Wayne and Wade Dickinson.

Radial well drilling is a *developed* technology for general applications. Radial well drilling technology has been tested at the pilot and field-scale levels for enhanced oil production. This research is being conducted by Petrolphysics, Ltd., and Bechtel Investments, Inc. of San Francisco, California.

Sources

Data on radial well drilling technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Wayne and Wade Dickinson, who are currently researching radial drilling; and Gene

Harris, USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of radial well drilling research.

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ULTRASONIC METHODS

Ultrasonic vibration is a technique that could increase the yields of recovery wells. Possible benefits from the application of ultrasonic vibration include:

- dispersing clay particles clogging pores adjacent to wells,
- reducing adsorption of contaminants onto the surfaces of clays,
- eliminating microorganisms clogging pores adjacent to wells.

Description

When ultrasonic vibrations are induced in a system composed of fluid and solid particles, they can result in cavitation on the surfaces of the particles. This phenomenon has been exploited in a wide range of industrial and laboratory applications.

Ultrasonic vibration is used extensively by soil scientists to disperse clay and silt particles in the laboratory (Edwards and Bremner, 1964 and 1967; Genrich and Bremner, 1972; Watson, 1971; Busacca and others, 1984; Busacca, 1986). In addition to dispersion, ultrasonic vibration is apparently a particularly effective method of removing mineral films or clay aggregates that may coat sand grains (Busacca and others, 1984).

The extraction of humic acid from soil was accelerated in the laboratory by placing the soil sample in an ultrasonic cleaner; Ramunni and Palmieri (1985) found that one hour of ultrasonic vibration gave results that were equal to or better than 24 hours of conventional agitation. Furthermore, Tamari and others (1982) reduced the time required to leach Na, K, Ca, Mg, Fe, and Mn ions from soils when they used an ultrasonic treatment, and Bertrand and Vukasovich (1977) observed an improvement in the cleaning of MoS_2 from steel surfaces when ultrasonic vibration was employed.

Ultrasonic devices designed to disintegrate cells and microorganisms for biological examination are commercially available (e.g., the high intensity ultrasonic probe manufactured by Sonicor Inc.). Although we are unaware of any previous applications of ultrasonic vibrations to specifically kill microorganisms, clearly the disintegration of cells from ultrasonics should result in an extremely high mortality rate for microorganisms.

The current applications of ultrasonic vibration suggest at least three ways the technique could be used to increase the recovery of contaminants from soils. One is the dispersion or disaggregation of clay particles, which could be used to clean the pores and increase permeability adjacent to boreholes by reducing the so-called "skin effect." Another is an increased ability to remove chemical species adhered to the solid particles, which could be used to improve recovery efficiency. A third is the sterilization of wells and elimination of microorganisms that clog neighboring pore spaces. This application could potentially eliminate the need to use antibacteriological chemicals to clear wells used in bioreclamation.

Documented Applications and Limitations

Ultrasonic methods appear to be applicable to sites where well yields are decreased by clay or microorganisms clogging soil pores in the vicinity of the well, or where contaminants near the well are bound to clays.

An experiment to determine if ultrasonic vibration would increase the permeability of a mixture of sand and clay in a small rigid-wall permeameter was conducted at the Center Hill Facility. Several falling head tests yielded consistent results of 3.8×10^{-4} cm/sec for the hydraulic conductivity of the sample. The effluent was clear water. When the permeameter was placed in an ultrasonic cleaner used for cleaning samples in the laboratory, another falling head test was conducted while the cleaner was turned on for 30 seconds. The results were immediate and impressive. The hydraulic conductivity increased abruptly to 1.8×10^{-3} cm/sec, and the effluent became a turbid mixture of clay and water. Thus, ultrasonic vibrations applied over a short period of time increased the hydraulic conductivity by a factor of four and dislodged clay particles so that they were removed by flow through the permeameter.

Status

Ultrasonic methods are a *conceptual* technology with the potential for recovery in remedial applications. Ultrasonic methods are not currently being investigated.

Ultrasonic methods are an *available* technology for general applications. Ultrasonic technology is routinely used for sample preparation in the biological and soil sciences and as a cleaner in certain industries. Current research into the applications of ultrasonic methods is being conducted by soil scientists such as Alan Busacca of Washington State University, Pullman, Washington.

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KERFING

Kerfing (or borehole notching) is a technique to cut a slot either normal or parallel to the axis of a borehole. Although recent interest in kerfing has been as a technique to help stop the migration of pollutants from uncontrolled waste sites, it may also have application as a recovery technique.

Description

Soil kerfing was developed in the United States and Europe although the first application was in Japan (Huck and others, 1980). It was originally intended to be used as a method to place impermeable barriers beneath hazardous waste sites to intercept leachate and prevent groundwater contamination (Huck and others, 1980).

Kerfing uses a high pressure jet of either water, water with entrained air, water and bentonite or water and an abrasive material, such as sand, to cut a slit in the wall of a borehole (Fig. 4). The jet is placed in a borehole and it is either rotated to cut a disk-shaped cavity, moved along the axis of the hole to create an axial slit, or kept in place to cut a cylindrical hole.

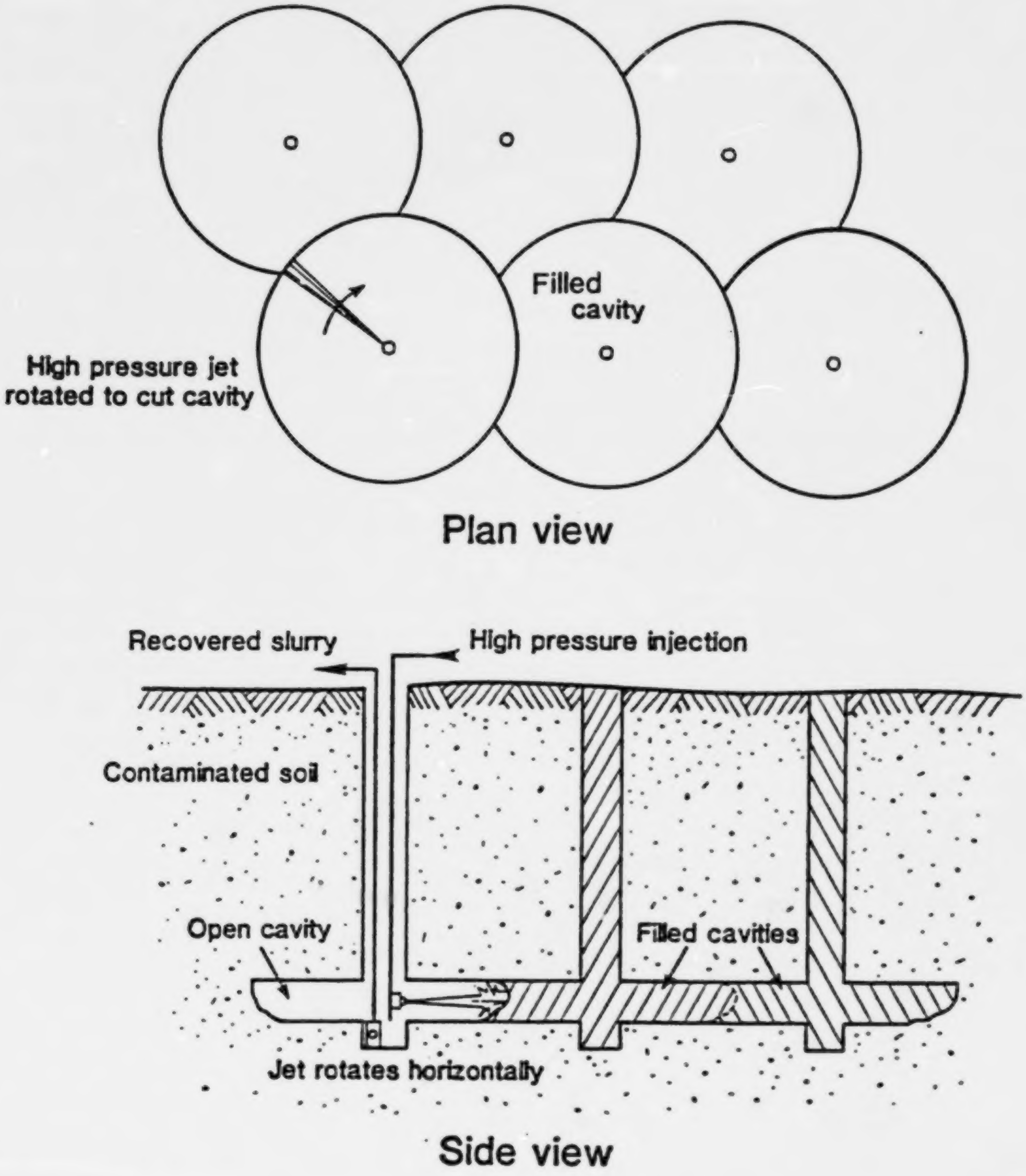
The jet advances the kerf at the rate of several centimeters to several tens of centimeters per second, and the final slit or hole is 1 to 3 meters long (Huck and others, 1980). Typically, jet pressures of 3000 to 30,000 psi are required to cut the kerf (Huck and others, 1980). The excavated slot is filled with either a permeable material to create a drain, an impermeable material to create a seal, or a remediating material to facilitate clean up (Fig. 4).

The cavity is held open with water or air pressure (May and others, 1985). Bentonite is added to cavities being cut in porous materials to form a water- and gas-tight seal on the walls of the cavity. The bentonite and the applied water or air pressure also aid in the removal of the cuttings from the borehole (May and others, 1985).

Two kerfing methods can be used to construct impermeable barriers. In one, a floor can be emplaced by kerfing a series of intersecting, disc-shaped cavities and filling them with bentonite slurry. This method is referred to as "pancake slurry jetting."

The other method uses kerfs to initiate hydraulic fractures. Two adjacent boreholes containing kerfs are simultaneously pressurized with a fracturing fluid (cement/grout) and fractures are generated that propagate outward from the kerfs. As the fractures approach each other, the stresses at their tips should tend to cause the fractures to intersect (Huck and others, 1980). Continued injection of the grout will form a continuous impermeable layer. This method was used to form a bottom barrier at a hazardous waste site in Florida (Brunsing, 1987)

Kerfing may also have application as a technique to improve recovery. One method of improving recovery might be to fill the kerf with a highly permeable material, much like a hydraulic fracture is filled with sand, which would improve the yield of the parent well.



Plan view

Side view

High pressure jet
rotated to cut cavity
Filled
cavity
Recovered slurry
High pressure injection
Contaminated soil
Open cavity
Filled cavities
Jet rotates horizontally

Figure 4. A high-velocity jet is used to cut a notch, or kerf, which can be filled with sand, bentonite slurry, or a remediating material. Filled cavities can overlap to form a continuous layer (after Huck and others, 1980).

Documented Applications and Limitations

Apparently, virtually any material can be cut with a kerfing tool; however Huck and others (1980) report that the "pancake slurry method" requires that the soil be free of cobbles too large to fall into the kerf. These cobbles produce zones of unkerfed soil, which results in an incomplete barrier.

In an evaluation of jet-grouting, The U.S. Army Corps of Engineers determined that cavities could be created in either silt or sand (May and others, 1985). However, the grout bulbs created were not always the size or shape needed to produce a continuous and complete barrier to contaminant movement (May and others, 1985).

Kerfing, as a recovery technique, appears to be most applicable to materials of low permeability, such as clay, silt or rock where groundwater flow is slow.

Although the increase in the rate of recovery from kerfing is undocumented, it would appear to be similar to that occurring after hydrofracturing. The rate could be expected to increase by a factor of two to ten, when compared with the rate before fracturing (Murdoch and others, 1987).

Status

Kerfing is an *emerging* technology with potential for both delivery and recovery in remedial applications. Kerfing technology is not currently being investigated.

Kerfing is an *available* technology for general applications. It is used routinely in the petroleum industry as a borehole notcher, assisting in the generation of hydraulic fractures. Halliburton Services Company and Dowell Schlumberger provide borehole notching services.

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Data on Kerfing technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Bruce Truett of the MITRE Corporation, McLean Virginia.

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ELECTRO-KINETICS

Electro-kinetics is a technology that has potential for delivering remediating materials and recovering spent solutions or contaminants, principally metals, from contaminated soil. Other possible applications to waste sites include the creation of hydraulic flow barriers and the injection of grout (Mitchell, 1986).

Description

Electro-kinetics has been used since the 1930's in construction projects to dewater and stabilize soils (Spangler and Handy, 1973). The same basic techniques and processes developed for dewatering and stabilization may have application to hazardous waste site remediation (Mitchell, 1986).

One electro-kinetic phenomena, electro-osmosis, occurs when a liquid migrates through a charged porous medium under the action of an applied electric field. Typically, the charged media is either clay, sand, or other mineral particles that usually carry negative surface charges (Fig. 5).

When charged particles are in contact with water, they attract positive ions that neutralize their negative surface charge. Consequently, cations predominate in the layer of water next to the surfaces of the particles forming what is known as the diffuse double layer (Renaud and Probstein, 1987).

An electric field applied through anodes to the saturated medium causes cations bound in the diffuse double layer to migrate towards negatively-charged cathodes. Viscous drag of water molecules by the cations causes a net flow of water towards the cathode. Basically, this is how the flow of water can be induced from the application of an electric field (Fig. 5).

Electro-osmosis generated by an externally imposed electric field occurs by means of a variety of electrochemical reactions at the electrodes by which charge is transferred through the porous medium.

The electrochemical reactions are critical because they convert the electron flow in the external metal circuit to ion fluxes in the porous medium (Gray and Olsen, 1986). The electrochemical reactions cause chemical changes to occur in the pore water, at the electrodes, and possibly on the surfaces of soil particles. Reduction occurs at the cathode primarily affecting the one or two species requiring the least energy potential (Segall and others, 1980). The principle cathodic reaction is the electrolysis of water and the subsequent reduction of hydrogen to form hydrogen gas.

The removal of hydrogen at the cathode decreases the hydrogen ion concentration; this results in an increase in hydroxide concentrations according to the common ion effect:

$$[H^+][OH^-] = K_W$$

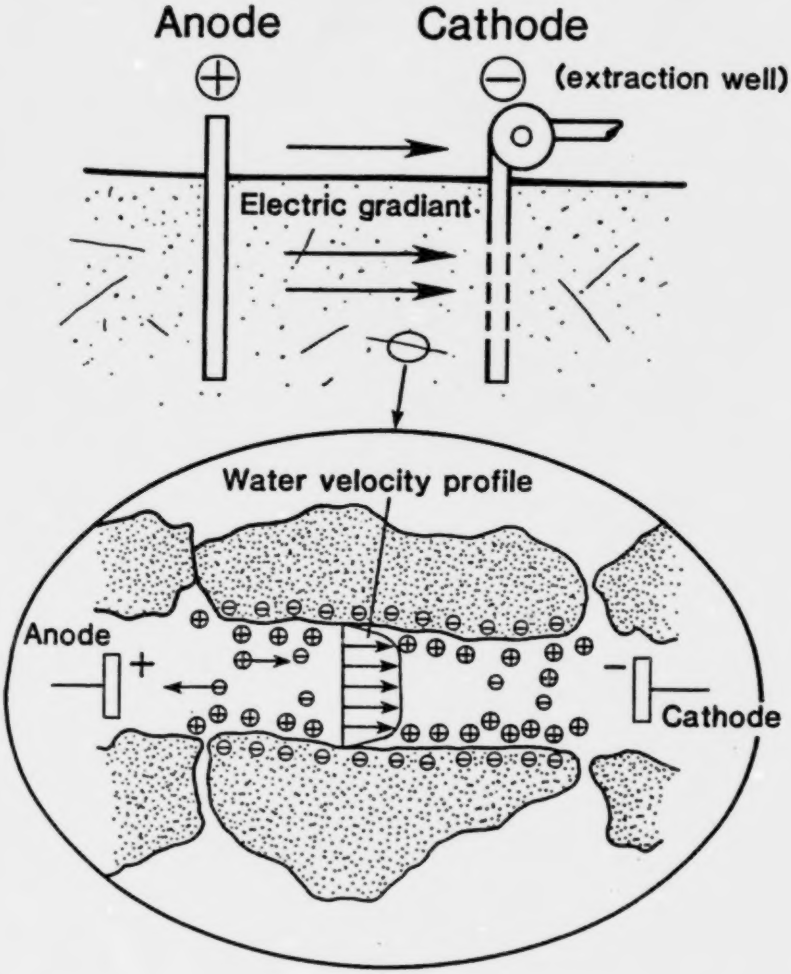
Anode
Cathode
(extraction well)
Electric gradiant
Water velocity profile
Anode
Cathode

Figure 5. Diagram of a hypothetical electro-kinetic operation. A direct current electrical field is applied to a contaminated soil to enhace the migration of contaminants to points of collection (after Renaud and Probstein, 1987).

where K_w = the equilibrium constant for the reaction. The pH of the system may exceed 13 (Segall and others, 1980).

Metallic anodes will be oxidized and supply electrons to the external circuit and cations to the surrounding media and oxygen gas may evolve at inert anodes through the electrolysis of water (Mitchell, 1986). Chlorine gas may also form from the reduction of chlorine ions in the vicinity of the anode (Segall and others, 1980).

Concentration gradients in the pore fluid will be established between the cathode and anode if unidirectional electrolysis is continued. These gradients cause diffusion from areas of high concentration to areas of low concentration that may be with or against the direction of ionic conductance transport.

Other electrochemical effects of importance are desiccation due to heat generation at the electrodes, mineral decomposition and the precipitation of salts and secondary minerals. These electrochemical effects can decrease the efficiency of the electrical treatment process.

One of the earliest and still widely used theoretical descriptions of electro-osmosis is the Helmholtz-Smoluchowski model. It is similar to Darcy's Law, so that methods used to solve groundwater flow problems can be used to estimate electroosmotic flow rates.

A crucial difference between groundwater flow and electroosmotic flow, however, arises from the independence of k_e (electroosmotic permeability) from hydraulic conductivity. Instead, electroosmotic permeability seems to depend on soil porosity and the zeta potential of the capillary walls, which appear to exhibit the most influence on electroosmotic permeability.

Thermodynamic models of the electroosmotic phenomena reveal that the efficiency of transport (amount of water moved per unit charge) depends on cation exchange capacity, water content and electrolyte concentration (Gray and Olson, 1986).

The efficiency of the electroosmotic system increases as the ratio of water to cation concentration (C_{H2O}/C^+) increases. The most efficient system is one where the cation exchange capacity (CEC) and salinity are low and the water content is high (Gray and Olsen, 1986).

A low CEC and high water content ensure that the ratio, C_{H2O}/C^+, is high. A low salinity helps exclude anions from the diffuse double layer. The greater the ratio of cations to anions the smaller the amount of energy required for the frictional drag of the cations and their water molecules to overcome the frictional drag of the anions.

The ability of electro-kinetics to dewater and stabilize soil has been well documented in the literature (Casagrande, 1953; Spangler and Handy, 1973; and Sowers, 1979). But the use of any electro-kinetic phenomena such as electro-osmosis as an in situ remediation technique is a new concept and research into its effectiveness is at an early stage.

Potential benefits of electro-osmosis are related to values of k_e. According to Gray and Olsen (1986), k_e usually ranges from 10^{-5} to 10^{-4} cm/sec per volt/cm and is generally independent of soil type. Thus, the rate of flow induced by the electro-kinetic technique in a well-sorted sand is expected to be similar to the rate in a tight clay. This phenomena makes electro-osmosis especially suited for the recovery of contaminants from soils of low to moderate permeability.

Documented Applications and Limitations

Electro-kinetics has been investigated in the field at a site (United Chrome Products Inc., Corvallis, Oregon) contaminated with chromium. That site was chosen for a field investigation because the nature of contamination and local hydrogeological conditions (nearly static ground water regime and a saturated, moderately permeable soil at shallow depth) were believed ideal to demonstrate this technology (Horng and others, 1987). Laboratory experiments on soil samples from the United Chrome site indicated that using electro-kinetics reduced the time of treatment compared with that needed for hydraulic leaching alone (Horng and others, 1987). Preliminary results from a subsequent series of field-scale tests at this site concur with the results of the laboratory experiments, again indicating reduced treatment time. The rates of recovery and resulting concentrations at the United Chrome site were unavailable during the preparation of this report.

Runnells and Larson (1986) showed, at the laboratory scale, that the application of an electric field can force a heavy metal (Cu) to migrate through groundwater. Approximately 53 percent of the original amount of the contaminant was removed from a test cell by electro-kinetics over a 30-day period.

Secondary effects of electro-kinetic treatment offer both advantages and limitations. Increases in pH that accompany treatment could, for example, facilitate the release of organic compounds to the soil water and promote recovery (Segall, 1986). Desiccation due to heating in the vicinity of electrodes, mineral decomposition, and the precipitation of salts and secondary minerals can, however, decrease the efficiency of the electrical treatment process.

Status

Electro-kinetics is a *developed* technology used for recovery in remedial applications. Electro-kinetic technology is being investigated at the pilot- and field-scale level at University of Washington in Seattle, Washington. The principal investigator is Sunirmal Banerjee.

Electro-kinetics is an *available* technology for general applications. Electro-kinetic technology is used as a construction technique to dewater and stabilize soil.

Sources

Data on electro-kinetic technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Jon Herrmann USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of electro-kinetic research.

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JET-INDUCED SLURRY METHOD

The jet-induced slurry method is a technique used to excavate an ore body by fragmenting subsurface material with a high-velocity hydraulic jet and then pumping the slurry through a borehole to the surface. This technology offers the unique capability of recovering solid material from the subsurface at depth without removing the overburden.

Description

The use of high-pressure water jets to slurry ore-bearing rock is by no means a new technique; it has been used for more than 100 years to mine placer gold and gilsonite at the ground surface. This technique has been applied to the subsurface, however, only within the past 20 years (Kasper and others, 1979).

Various types of jet-induced slurry mining methods (termed "in situ borehole slurry mining" by the mining industry) have been developed over the years (Savanick, 1987). These techniques typically involve drilling an 18-inch diameter borehole to slightly beyond the bottom of the ore-bearing horizon and casing from the top of the ore-bearing horizon to the ground surface. A borehole-mining tool (BMT) is lowered down the hole. The BMT generates a high-velocity water jet that erodes and slurries the ore. The slurried ore is drawn into an inlet in the BMT and pumped to the surface. The ore is processed at the surface and the tailings can be used to backfill the cavity left by the excavation. Backfilling significantly reduces the possibility of future surface subsidence (Fig. 6; Kasper and others, 1979).

To mine the ore, the jet is rotated perpendicular to the BMT while the BMT is moved upward. The jet can be fully rotated through an arc of 360^{o} or rotated through a lesser arc that leaves a portion of the ore body for roof support. Material can be removed up to 75 feet from the borehole depending on the properties of the ore body and the jet system.

Documented Applications and Limitations

Lithified sediments, such as pebble phosphate deposits in Florida and North Carolina and uranium-bearing sandstones in Wyoming and Texas, have been mined using this technique (Kasper and others, 1979). Ore bodies located above and below the water table have been mined using borehole slurry mining (Kasper and others, 1979).

Recently the U.S. Bureau of Mines developed a prototype borehole-mining tool (Savanick, 1987). The BMT was first tested at Wilkeson, WA on a steeply dipping coal seam. The BMT removed an average of 8 short tons/hour (st/h) at depths ranging from 25 to 75 ft (Savanick, 1987). The BMT was also tested on an uraniferous sandstone in Natrona County, Wyoming. An average of 8 st/h were removed from depths ranging from 75 to 100 ft (Savanick, 1987).

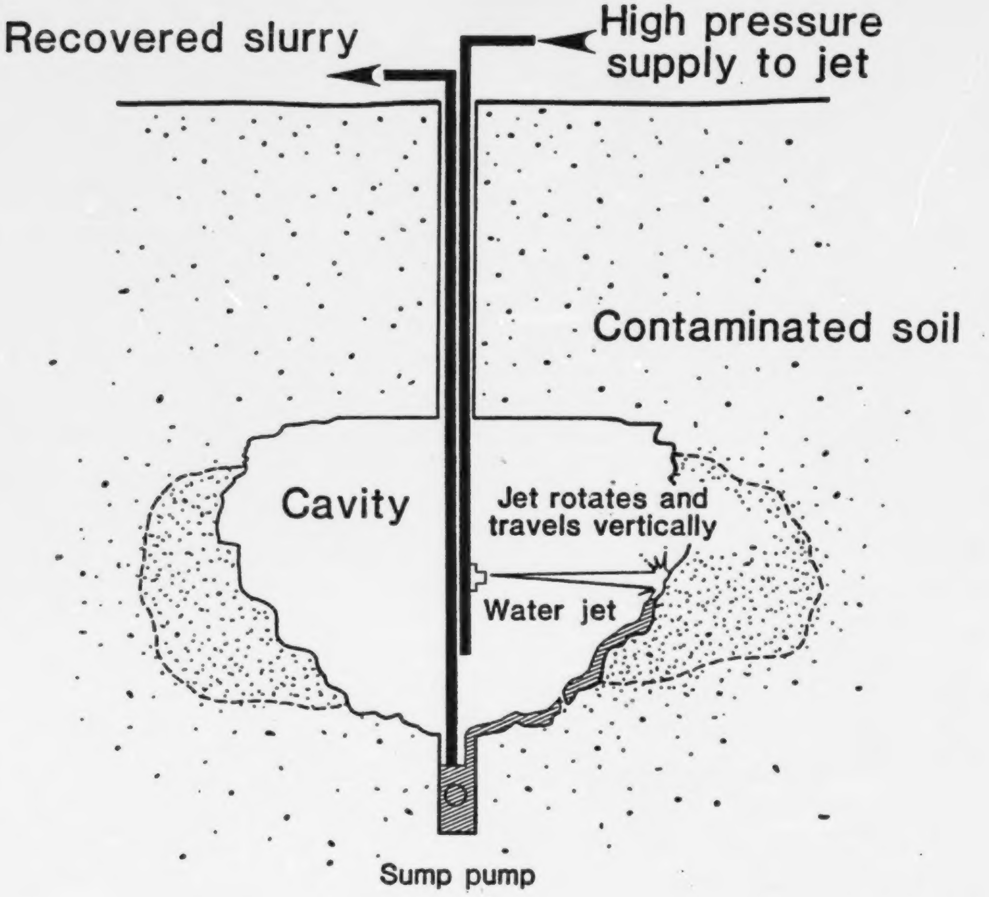
Recovered slurry
High pressure supply to jet
Contaminated soil
Cavity
Jet rotates and travels vertically
Water jet
Sump pump

Figure 6. Schematic of a jet-induced slurry operation. A jet cutting tool is used to fragment the contaminated medium, which then flows through the excavated cavity, and is pumped to the surface as a slurry (after Kasper and others, 1979).

In 1979 at Kern County, California, one thousand short tons of oil sand were mined at a rate 14 st/h from depths ranging between 110 and 150 ft (Savanick, 1987). Between April and August 1980, 1700 short tons of phosphate ore were produced from depths ranging from 230 to 250 ft in St. Johns County, Florida. The average production rate was 25 st/h (Savanick, 1987).

Status

Jet-induced slurry method is a *conceptual* technology that could potentially be used for recovery in remedial applications. Jet-induced slurry method technology is not currently being investigated as a remedial technique.

Jet-induced slurry method is a *developed* technology for general applications. Jet-induced slurry method technology is being developed and tested to mine an ore body at depth without the removal of overburden. Continuing research is being conducted at Halliburton Services Company and the U.S. Bureau of Mines.

Sources

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CARBON DIOXIDE INJECTION

Carbon dioxide is injected into oil-bearing rock formations to maintain pressure and displace oil. The two principle mechanisms by which carbon dioxide mobilizes oil are (1) the reduction oil viscosity upon solution of the gas into the oil and (2) the maintanence of reservoir pressure with the increase fluid volume in the reservoir upon CO_2 injection(Holm, 1987; Donaldson and others, 1985; Morrow and Heller, 1985).

Carbon dioxide flooding to recover groundwater contaminants would likely be limited to applications where carbon dioxide is either dissolved in water or contained in aphrons. In either case, carbon dioxide could be used to decrease the viscosity and increase the recovery of hydrocarbons.

Description

Injecting carbon dioxide at high pressures (about 1200 psi) increases the solubility and dramatically reduces the viscosity of the oil (Grogan and Pinczewski, 1987; Holm, 1987; Collins and Wright, 1985; Latil, 1980).

Reducing the viscosity of oil results in two phenomena that increase recovery: decreased viscosity increases oil mobility, thereby decreasing the head gradient required to sustain flow; and when the contrast in viscosity between oil and the displacement fluid is decreased, the formation of viscous instabilities, or fingers is minimized (Holm, 1987; Donaldson and others, 1985).

The most commonly used method of carbon dioxide injection is the water-alternating-gas (WAG) method, in which a carbon dioxide slug is followed by alternate water and carbon dioxide injections. Another method involves injecting water saturated with carbon dioxide. The third method consists of high-pressure injection of the gas itself (Fig. 7; Holm, 1987; Donaldson and others, 1985; Latil, 1980).

Documented Applications and Limitations

Carbon dioxide injection is effective for relatively low oil viscosities, ranging from 0.2 to 7 centipose (cp). Maximum oil viscosity is 12 cp. Oil densities of 0.9 g/cm^3 are common. Gas flooding works best for recovery of oils with high specific gravity (> 30^o API) (Collins and Wright, 1985).

Carbon dioxide gas pressures are typically around 2000-3000 psi for reservoirs buried several thousand feet deep. Minimum pressure is 1100 psi, or about 2300 ft, in the field (Collins and Wright, 1985), although laboratory studies show minimum carbon dioxide pressures as low as 700 psi (Fischer and others, 1984). Reservoir temperature is not a critical factor (Holm, 1987; Collins and Wright, 1985).

Successful carbon dioxide injection programs have been implemented in limestones and dolomites with 10 to 15 percent porosity and 5-25 md permeability

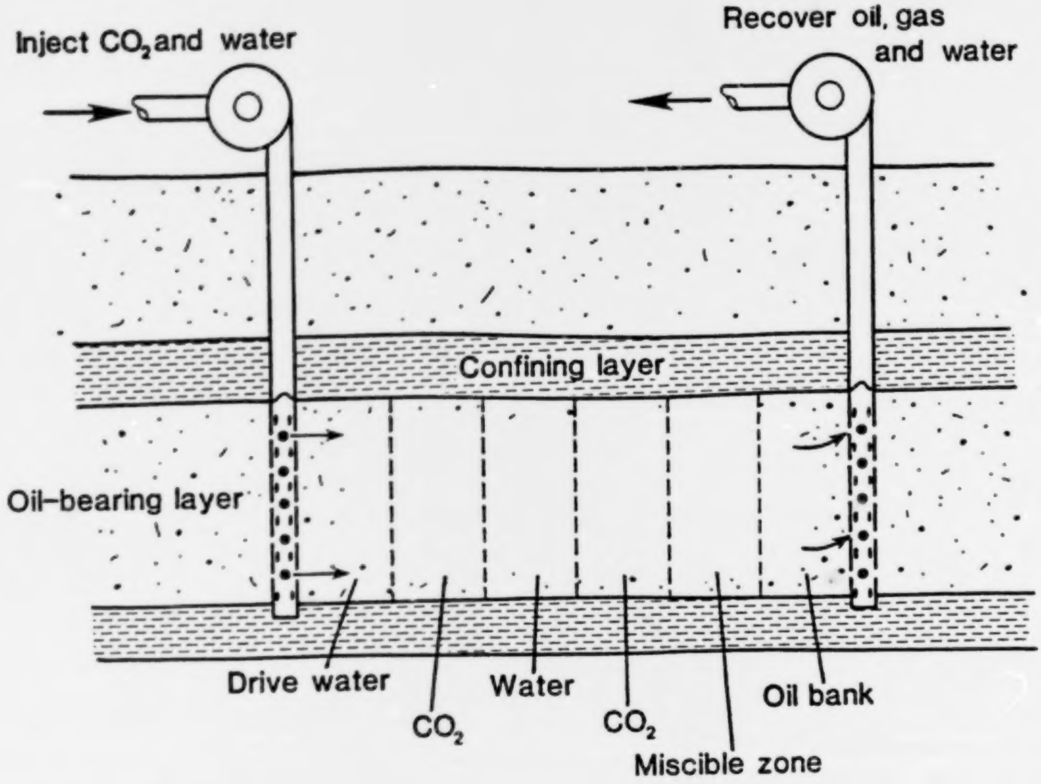
Inject CO_2 and water
Recover oil, gas and water
Confining layer
Oil-bearing layer
Drive water
CO_2
Water
CO_2
Oil bank
Miscible zone

Figure 7. Schematic diagram of carbon dioxide flooding, in which alternating slugs of carbon dioxide and water are injected (after Donaldson and others, 1985).

(Pittaway and others, 1987; Albright, 1986; Pittaway and others, 1985; Ader and Stein, 1984); and in sandstones with 10 to 35 percent porosity and 10 to 1500 md permeability (Williamson and others, 1986; Bolling, 1985; Boyer, 1985; Cardenas and others, 1984; Palmer and others, 1984). There do not appear to be any lower limits for either permeability or porosity. Homogeneous permeability distribution is preferred, but unnecessary (Collins and Wright, 1985).

Generally, less than 5 percent of the residual oil is left behind in reservoir rock after carbon dioxide injection (Holm, 1987; Fischer and others, 1984).

The volumetric ratio of carbon dioxide injected to oil recovered ranges from 0.1 (Williamson and others, 1986; Desch and others, 1984; Ehrlich and others, 1984) to several hundred (Bolling, 1985; Boyer, 1985). Reservoirs depleted to less than 10 percent of the original oil in place have overall injection-to-recovery ratios of 0.09 to 0.1 (Williamson and others, 1986; Desch and others, 1984).

Rates of injection of carbon dioxide range from tens to ten-thousands of m^3/day (Pittaway and others, 1987, 1985; Bolling, 1985), whereas oil recovery rates range from tens to thousands of cubic meters per day (Williamson and others, 1986; Pittaway and others, 1987, 1985; Desch and others, 1984).

Status

Carbon dioxide injection is a *conceptual* technology potentially used for recovery in remedial applications. Carbon dioxide injection technology is not currently being investigated.

Carbon dioxide injection is an *available* technology for general applications. It is used routinely in enhanced oil recovery to maintain reservoir pressure and reduce oil viscosity.

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POLYMER INJECTION

Water-soluble polymers are added to waterflooding solutions in the petroleum industry to (1) increase the viscosity of flooding fluid, thereby decreasing the viscosity contrast between the oil and flooding fluids, or (2) form highly viscous gels in situ (to homogenize reservoir permeability).

The homogenization of permeability is one possible application of polymers for the recovery of contaminants. Temporarily filling high-permeability channelways with polymer gels could be used to induce flow and transport contaminants out of local zones of low permeability.

Description

Polymers are used to increase the viscosity of injected water, and hence, to reduce the mobility contrast between injected water and reservoir oil. (The mobility of a phase is defined as the ratio of the effective permeability to the viscosity.) A polymer-augmented, or thickened, waterflood tends to move more oil without allowing the flood to form viscous instabilities, or fingers, through the oil.

With early forms of polymer flooding, the polymers had to be constantly injected because they were being continuously flushed out of the system with the water. Recently, however, polymers such as polyacrylamides have been crossed with metallic ions, such as aluminum to form a gel that sets up in-place within fractures or high-porosity zones (Burkholder and Withington, 1987; Mumallah, 1987). The cross-linked polymer gel effectively homogenizes the reservoir, and it remains in-place for over 100 hours according to laboratory tests (Mumallah, 1987). Other polymer gels are based on xanthan gums (Burkholder and Withington, 1987; Kohler and others, 1987).

Eliminating or reducing localized, high-permeability zones, either by polymer injection or in situ precipitation of a polymer gel, is of critical importance to ultimate oil recovery (measured in percent recovery of the original oil). This is because the highest oil saturation is in the low-permeability zones that are missed by ordinary waterfloods because the water is preferentially diverted into high-permeability, low-oil-saturation "thief zones." Such thief zones must be treated with permeability-reducing gels to maximize the efficiency of recovery (Needham and Doe, 1987; Gogarty, 1983a,b).

To effect polymer injection, a preflush is usually used to place a compatible aqueous buffer between the highly saline reservoir brine and the chemical solutions, which may be adversely affected by the dissolved salts. The preflush should remove most of the divalent cations (calcium and magnesium) that were in the pore-filling brine, since many polymer solutions react with such cations (Fig. 8). Freshwater is often used as a preflush. Some polymer solutions, however, are brine-tolerant, eliminating the need for a preflush (Collins and Wright, 1985).

A surfactant solution is injected after the preflush, but before the polymer solution, to release oil in situ (Fig. 8). The surfactant solution is a micellar substance that reduces

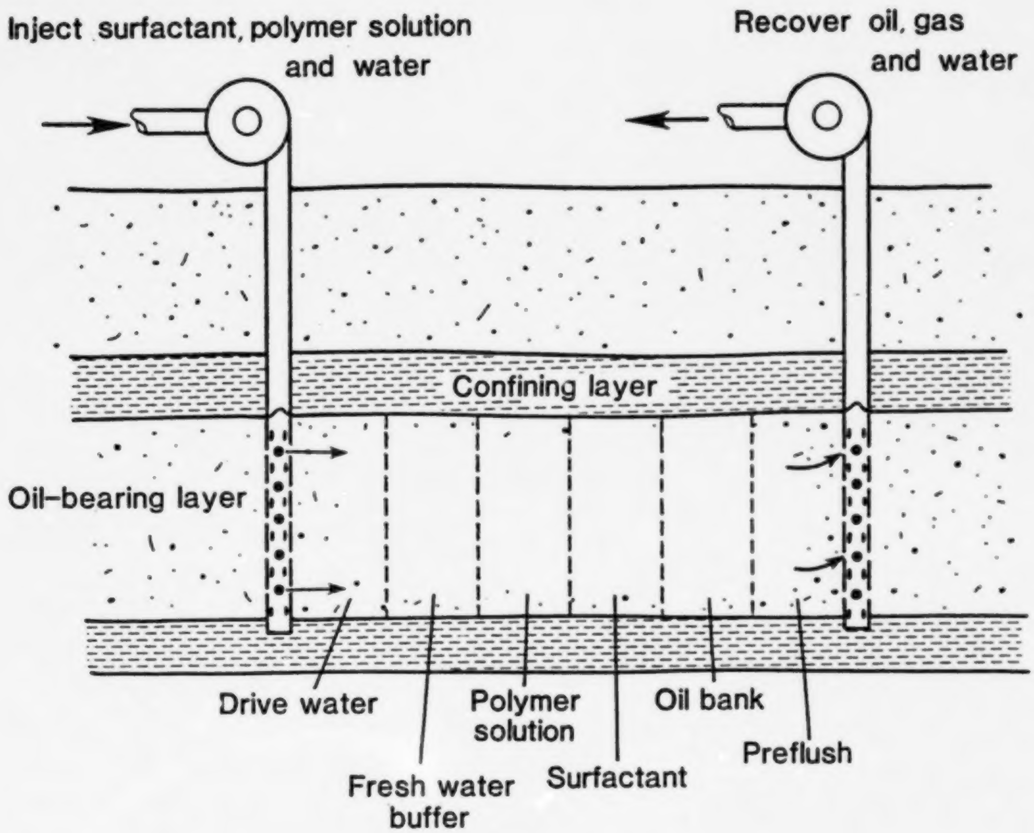
Inject surfactant, polymer solution and water
Recover oil, gas and water
Confining layer
Oil–bearing layer
Drive water
Polymer solution
Oil bank
Preflush
Fresh water buffer
Surfactant

Figure 8. Schematic diagram of micellar-polymer injection. The preflush serves as a buffer between the saline reservoir and the polymer solution. The surfactant solution is an alkaline, micellar agent that releases oil by reducing the interfacial tension between oil and water (after Donaldson and others, 1985).

the interfacial tension between water and oil (Collins and Wright,1985; Dreher and Shoppman, 1985) and hence releases oil that either coats pore walls or forms blobs too large to pass through narrow pore throats (Andersen, 1987; Morrow and Heller, 1985; Trantham, 1983).

Documented Applications and Limitations

Polymer injection has been applied to both sandstone and carbonate reservoirs. The presence of clay minerals does not present major obstructions to the effectiveness of polymer flooding (Kantorowicz, 1988). Oil viscosities may be as high as 200 cp, and specific gravity of the oil should be greater than 18° API for the technique to be worthwhile. Polymer injection has been shown to withstand temperatures of up to 200°F. Reservoir thickness and pressure are not critical factors (Collins and Wright, 1985; Norman and others, 1984).

Porosity by itself is not a critical factor, as long as the permeability is greater than 50 md. Porosity may be strongly heterogeneous (Collins and Wright, 1985; Tinker, 1983).

With polymer/surfactant flooding, about 40 to 70 percent of the in-place oil can be economically recovered, under favorable conditions (Doll and Hanson, 1987; Needham and Doe, 1987; Barnes and Tinker, 1985; Collins and Wright, 1985; Langston and Shirer, 1985; Mack and Warren, 1984; Gogarty, 1983a).

The volumetric ratio of polymer-augmented water injected to oil recovered ranges from 16 to 50 for simple polymer floods; this is up to five times greater than the same ratio for surfactant-polymer floods (Doll and Hanson, 1987; Barnes and Tinker, 1985; Collins and Wright, 1985; Mack and Warren, 1984).

Injection rates are typically about 50 to 100 m^3/day of solution, polymerized with about 0.2 to 0.5 kg of polymer per m^3 of water (Doll and Hansen, 1987; Mack and Warren, 1984; Tinker, 1983).

Status

Polymer injection is a *conceptual* technology potentially used for recovery in remedial applications. Polymer injection technology is not currently being investigated.

Polymer injection is an *available* technology for general applications. Polymer injection technology is used routinely in enhanced oil recovery techniques to increase the viscosity of the flooding fluid and homogenize the permeability of the reservoir. Current research is focused on the development of cross-linked polymer gels that form in situ.

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VAPOR EXTRACTION

A vapor extraction system (VES) involves the recovery of vapor-ladened air from unsaturated soils by applying a vacuum at extraction wells. The process appears to be limited to those contaminants that exhibit significant volatility at ambient temperatures.

Description

Vapor extraction techniques used at hazardous waste sites to remove volatiles from contaminated soil have been adapted from the solid waste disposal industry where control, treatment, and recovery of methane is a long-practiced technique (Hutzler, 1987; AFESC/RDV, 1988). Vapor extraction is currently the most commonly used in situ remedial technology (AFESC/RDV, 1988).

The pore space of unsaturated soils is composed of liquid and vapor phases that are assumed to be in equilibrium. Compounds with moderate to high vapor pressures will be partitioned more strongly into the vapor phase than compounds of lesser vapor pressure.

The vapor extraction technique makes use of the strong partitioning by removing the vapor phase from the soil through application of a vacuum at well points. Pressure gradients are established within the soil to induce convective air flow through the porous media (Glynn and Fan, 1988). Consequently, liquid phases volatilize to maintain local equilibrium between liquid and vapor (Woodward-Clyde, 1985). By removing only vapor, it is possible to reduce or even eliminate some liquids from the soil.

Vapor extraction systems use wells to apply the vacuum to contaminated media. The applied vacuum induces air flow through the media and removes the vapor phase. Air-inlet wells have been used to enhance vapor extraction by allowing continued air flow and contaminant volatilization (Fig. 9; Bennedsen and others, 1987). To fully decontaminate a soil it may be necessary to reverse well functions (Woodward-Clyde, 1985).

Documented Applications and Limitations

Vapor extraction units can be installed in virtually any unsaturated media regardless of the depth to ground water (Malot, 1985). Recovery systems have been installed in clay-rich soils, sands, and fractured rock (Malot, 1985). Grain size, stratification, and moisture content are important variables that affect the conductivity of the soil to vapor. Heterogeneities in soil composition and the development of preferred flow paths tend to retard the vapor extraction process.

The rate of extraction affects the amount of volatile organic compounds removed. Thornton and Wootan (1982) note that high extraction rates maximize concentration gradients, encouraging the diffusion of the contaminant vapor away from the contaminant-air interface, and thereby promoting the volatilization and removal of the contaminant. The rate at which vapor is removed is a function of the volatility, solubility,

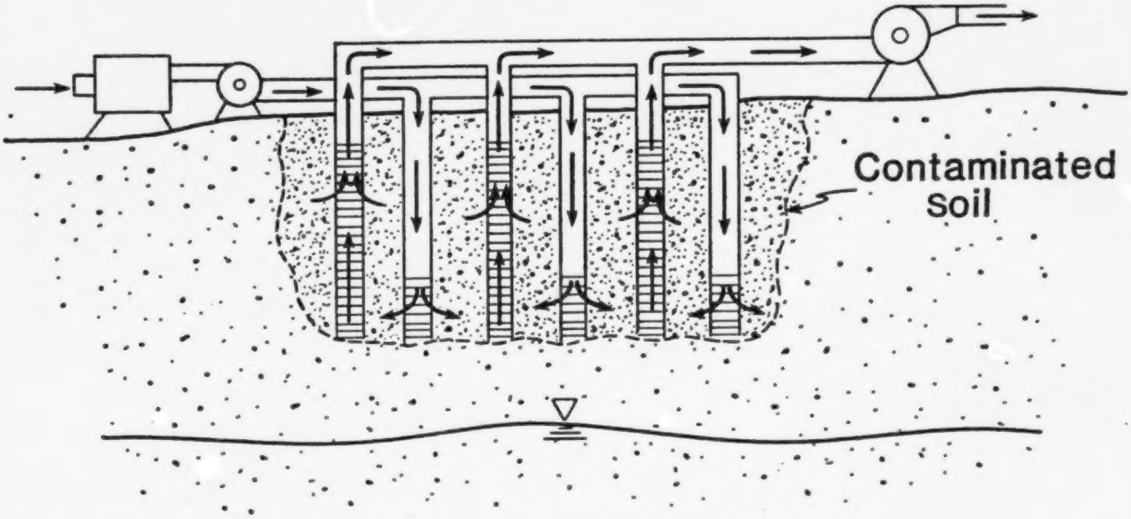

Figure 9. Diagram of a typical vapor extraction operation. Here air is continuously injected into the contaminated, unsaturated soil while vacuum extraction wells remove air and organic compounds (after Anastos and others, 1987).

adsorption characteristics, and initial distribution of contamination. Vapor extraction only removes significant quantities of compounds that are moderately to highly volatile, compounds with vapor pressures over 0.5 mm of mercury at 20^{o}C or those with values of Henry's Law constants greater than 0.01 (Bennedsen and others, 1987; Hutzler, 1987).

Compounds that have been effectively extracted include gasoline, diesel fuel, hexane, benzene, toluene, ethyl benzene, carbon tetrachloride, chloroform, methylene chloride, tetrachloroethane, trichloroethane, tetrachloroethylene, trichloroethylene, dichloropropene, chlorobenzene, hexachlorobenzene, acetone, methylethyl ketone, and methanol (Malot, 1985; AFESC/RDV, 1988).

The performance of VES in remediation can be estimated from preliminary results of recent field tests. A Terra Vac, Inc. VES was used at a site outside of San Juan, Puerto Rico, to remediate a clay-rich soil contaminated with carbon tetrachloride. Once fully operational, the system extracted 250 lbs of carbon tetrachloride per day. After 30 months the VES had recovered more than 70 percent of the spilled volume (Agrelot and others, 1985).

Terra Vac's VES was also used to cleanup soil contaminated by a leaking underground storage tank. At least 10,000 gallons of gasoline had been released to the subsurface from a service station located 600 ft up-gradient of a drinking water wellfield in Belleview, Florida. The VES was installed and used to recover 8000 lbs. of hydrocarbons over a three week test period at rates ranging from 450 to 2000 lbs/day (Applegate and others).

Terra Vac's process is currently undergoing field demonstration testing at a site in Groveland, Massachusetts under the auspices of the Superfund Innovative Technology Evaluation (SITE) program (Michaels and Stinson, 1988).

Nunno and others (1987) report that a VES removed 70 kg of chlorinated hydrocarbons in 4 months at a contaminated site in the Federal Republic of Germany. The system may also have had an effect on contaminant concentration in the groundwater below the site, lowering the concentration from 5,400 mg/kg to 205 mg/kg in one well, while slightly increasing the concentration in another.

At another site, 73 kg of tetrachloroethylene (PERC) was extracted by a VES during 35 days of operation (Payne and others, 1986). The levels of PERC in soil samples taken 10 feet below ground surface dropped from 700 mg/kg to 0.84 mg/kg and levels taken from 15 feet below ground decreased from 5,600 mg/kg to 0.64 mg/kg after 45 days of operation.

After 3 years of operation, approximately 12,000 lbs of volatile organic compounds were removed from contaminated soil at a site in California using a VES (Bennedsen and others, 1987). And at an ammunition plant in Minnesota, extraction rates of total volatile organics exceeded 36 lbs/day from contaminated soil (Weston, 1985).

Status

Vapor extraction is a *developed* technology used for recovery in remedial applications. Vapor extraction technology is being and has been investigated at the bench-, pilot- and field-scale levels by various consultants and academicians. Investigators include Neil Hutzler of the Michigan Technological University, Houghton, Michigan and the consultants: Woodward-Cylde of Walnut Creek, California, Roy Weston of West Chester, Pennsylvania, AWARE Inc. of Nashville, Tennessee, Midwest Water Resources, Michigan and Terra Vac of San Juan, Puerto Rico.

Techniques similar to vapor extraction are *available* for general applications. These techniques are used by the solid waste management industry to control, treat, and recover methane generated at landfills.

Sources

Data on vapor extraction technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Paul DePercin, USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of vapor extraction research and Mary Stinson of USEPA HWERL, Edison, New Jersey and representatives of Terra Vac, San Juan, Puerto Rico.

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STEAM STRIPPING

In situ steam stripping is a method intended to recover not only highly volatile but also moderately low vapor pressure organic compounds from contaminated soil. The rate of vaporization and transport of these compounds increases as a result of increasing soil temperature following contact with the steam. The steam has two main functions: it vaporizes the contaminants and it becomes the transport medium for the vaporous materials. A partial vacuum (underpressure) can accelerate the rate of volatilization and speed the transport of contaminants to collection points.

Description

Steam stripping techniques have been used by the petroleum industry for more than 30 years to recover hydrocarbons from coal beds, tar sands, or asphalt deposits. A typical steam stripping operation used in the petroleum industry involves three stages (Arscott and David, 1977):

1) delivering steam via injection wells to a target zone;

2) heating the target zone either to vaporize volatile organics occurring above the water table or to reduce the viscosity of organic liquids occurring below the water table; and

3) creating a pressure gradient that induces flow of organic compounds to recovery wells.

The oil industry employs two standard methods of steam stripping: steam flooding and steam stimulation (Blevins and others, 1984). In the most commonly used method, steam flooding, steam is injected into a central well and water and organic compounds are recovered (at or near ambient subsurface temperatures) at peripheral recovery wells (Fig. 10).

Steam stimulation or cyclic injection is a single well injection and recovery scheme whereby steam is injected into the target horizon and allowed to sit or soak for a given period of time. Water and organic compounds are then recovered through the same well used for steam injection. The introduction of heat coupled with the soaking period reduces the viscosity of the organic compounds and enhances production. The well is pumped until production decreases significantly, and then the procedure is repeated (Fig. 10).

Steam stripping has been used in the environmental field to recover volatile organic compounds (VOC's) from aqueous waste streams (USEPA/625/8-87/014; Branscome and others, 1987) and excavated soils (Olexsey and others, 1987). Recently, steam injection has been investigated as an in situ treatment technique for soils contaminated with VOC's (Lord and others, 1987a).

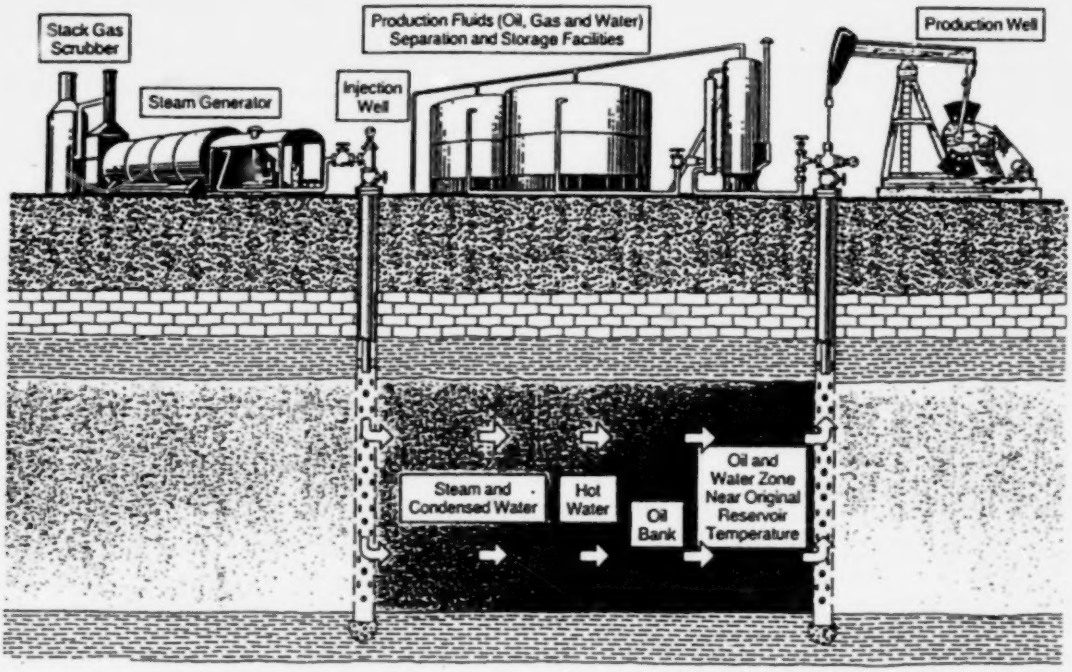
Stack Gas Scrubber
Steam Generator
Production Fluids (Oil, Gas and Water) Separation and Storage Facilities
Injection Well
Production Well
Steam and Condensed Water
Hot Water
Oil Bank
Oil and Water Zone Near Original Reservoir Temperature

Figure 10. Schematic of a typical steam stripping operation used in the petroleum industry. Heat from the injected steam reduces the viscosity and increases the mobility of the hydrocarbons. (after Donaldson and others, 1985).

Volatile organic liquids will vaporize when the thermal energy of the steam exceeds the heat of vaporization of the liquid. As the steam condenses, the latent heat that is released causes soil temperatures to increase thereby mobilizing contaminants that would be immobile at ambient temperatures (Hilberts and others, 1985). In general, in situ steam stripping can be used to recover most organic contaminants with boiling points below 250°C (Hilberts and others, 1987).

In contaminant steam stripping of liquid mixtures, when the sum of the partial pressures of the contaminants and water exceeds ambient barometric pressure, the mixture boils and the contaminants come off with the steam. The quantity of each material distilled from the soil at the stripping temperature is proportional to the product of the molecular weight and partial pressure of each constituent. Thus, for the low volatility components (usually those with higher molecular weights), the effective vapor pressure is adjusted upwards by the higher molecular weight, such that there is more effective removal of the higher boiling components than would be possible due only to distillation in the absence of steam (Brugger pers comm, 1988).

Once volatile liquids have been vaporized, the combination of wet steam and organic vapor must be recovered. Recovery is accomplished from the subsurface using extraction wells, or at the ground surface using an innovative geosynthetic cap placed over the site. Typically, a cap consists of a high transmissivity geotextile and a flexible membrane liner containing several outlet ports. Suction is applied to the underside of the liner and vapor or liquid flows through the geotextile beneath the liner to the outlet ports (Lord and others, 1987b).

The flow from the outlet ports is condensed or otherwise trapped and treated by conventional liquid/vapor state remediation processes. Recent, small-scale experiments in a 1 ft x 1 ft x 1 ft soil-filled box show that the geosynthetic cap is an effective collector of contaminants stripped from the soil (Murphy, 1988).

Recovery of wet steam and organic vapor can also be accomplished with extraction wells designed to maintain a negative pressure head in the soil. The underpressure causes a lowering of the boiling points of the contaminants that, in conjunction with the induced pressure gradient, accelerates vaporization and recovery (Hilberts and others, 1985).

Preliminary laboratory work was completed for steam-front behavior in various soil types (Lord and others, 1987b). In these experiments, the wet steam front migrated uniformly in sand and silty sand soils (Lord and others, 1987b). The rate of migration decreased as silt content increased and permeability decreased. In a soil of 100 percent silt, the steam front migrated nonuniformly, with preferential flow along fractures believed to be induced by the steam (Lord and others, 1987b).

A rough estimate of the steam hydraulic conductivity (K_{steam}) for sand and silty sand soil was made by Lord and others (1987b). It was determined that K_{steam} was of the same general magnitude as K_{water} (hydraulic conductivity of the soil to liquid water). A more recent investigation (Lord and others, 1988) yielded determinations of these two permeabilities and confirmed that they are of the same general magnitude.

Supercritical fluid extraction, a phenomena related to steam stripping, has been investigated for the removal of organic chemicals from excavated soils (Brady and others, 1985). In general, the supercritical phase of a fluid is achieved by increasing the temperature above that required to achieved the vapor phase. The method is effective because supercritical fluids--water or carbon dioxide, in particular--are excellent solvents for organic chemicals. Unfortunately, the relatively high pressures and temperatures required to maintain fluids in a supercritical state appear, at present, to preclude the use of this technique in the subsurface.

Documented Applications and Limitations

Steam stripping is limited to those organics that are highly to moderately volatile (Hwang and Fahrenthold, 1980). Contaminants removed during field tests include: benzene, ethyl benzene, nephthalene, phenol, toluene, and xylene (Hilberts and others, 1985).

Hilberts and others (1985) report that steam stripping removed up to 95 percent of benzene, ethyl benzene, toluene, and xylene contaminating a sandy soil. The technique removed 60 percent of naphthalene contaminating a clay and 99 percent of naphthalene contaminating a sand. Steam stripping removed 80 percent of the phenol contaminating a sand and clay. At a former gasworks in Mannheim, Germany, soil contaminated with benzene (55 mg/kg), phenol (30 mg/kg), and toluene (15 mg/kg) was treated by steam stripping and all contaminant concentrations were reduced to undetectable levels (Hilberts and others, 1985).

Toxic Treatment (USA) Inc. has developed a mobile in situ soil mixing and steam stripping unit (The Detoxifier) to remediate soils contaminated with hydrocarbons (La Mori and Ridosh, 1987). The Detoxifier uses two overlapping augers 5 feet in diameter to simultaneously inject steam, hot air and/or an oxidizer while mixing and pulverizing the soil (Treweek and Wogec, 1988). Escaping vapors are captured in a surface shroud and then condensed and removed. This system is capable of treating soils to depths of 25 feet (Treweek and Wogec, 1988).

The Detoxifier was used to remediate 4700 cubic yards of unsaturated soil contaminated with petroleum hydrocarbon compounds (La Mori and Ridosh, 1987). In the northern portion of the site where hydrocarbon concentrations were 1000 ppm or less removal efficiencies of 75-90 percent were usually achieved in only 47 minutes (La Mori and Ridosh, 1987). In the southern portion of the site initial hydrocarbon concentrations averaged 10,000 ppm. Here, removal efficiencies of 90-95 percent were achieved in an average treatment time of 78 minutes (La Mori and Ridosh, 1987).

Although soil permeability would not appear to be a factor for The Detoxifier, permeability and the degree of saturation of the contaminated medium do limit effectiveness of steam stripping. Laboratory and field tests indicate that soils composed largely of sand (with varying amounts of silt and clay) are permeable enough for successful steam stripping (Hilberts and others, 1985; Lord and others, 1987b). The degree to which the soil is saturated may affect the rate of steam migration and contaminant removal. Soil water provides an extra source of steam that buffers pressure changes and may cause large delays in steam-front propagation (Herkelrath and others, 1983).

Status

Steam stripping of contaminated soil is a *developing* technology used for recovery of organic contaminants in remedial applications. Steam stripping technology is being investigated at the bench- and pilot-scale levels at Drexel University in Philadelphia, Pennslyvania. Principal investigators include Arthur Lord, Robert Koerner and Vince Murphy. The Detoxifier is available from Toxic Treatment Inc., San Matea, California.

Steam stripping is an *available* technology for general applications. Steam stripping technology is used routinely in the petroleum and mining industries to strip hydrocarbons from coal beds, tar sands, and asphalt deposits.

Sources

Data on steam stripping technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Arthur Lord, who is currently researching steam stripping; and John Brugger, USEPA HWERL, Edison, New Jersey, who is project officer for Cooperative Agreement No. CR-813022 on steam stripping research.

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HOT-BRINE INJECTION

Large quantities of natural gas exist as solid gas-hydrate deposits. Production of solid or even liquid phases is more difficult than production of a vapor phase, so petroleum engineers have developed methods of driving the phase change from solid or liquid to a vapor (Kamath and Godbole, 1987). Hot-brine injection increases both temperature and salinity to promote dissociation reactions that drive solid or liquid gas-hydrates into a vapor phase and water (Fig. 11; Kamath and Godbole, 1987).

Hot-brine injection could be used at uncontrolled hazardous waste sites to recover certain contaminants whose dissociation temperatures decrease with an increasing salinity of pore fluid. The applicability of this method will require a salinity dependence on the dissociation temperature of the contaminant species to be recovered.

Description

The application of the hot-brine method to recover natural gas hydrates appears to be limited to depths greater than 150 meters because the hydrate equilibrium curves show lower dissociation temperatures than ambient earth temperatures at shallow depths (Kamath and Godbole, 1987).

At burial depths of about 150-1000 meters, the temperature of hydrate dissociation from a solution with zero salinity exceeds the ambient temperature of the surrounding earth by almost 10°C. Increasing the salinity of the pore fluid from 0 to 15 weight percent reduces the temperature of hydrate dissociation by about 11°C, the relationship between salinity and dissociation temperature reduction is approximately linear within the 0 to 15 weight percent salinity range (Kamath and Godbole, 1987).

The heat required to dissociate gas hydrates into a vapor phase and liquid water decreases with decreasing dissociation temperature. Increasing the salinity of the pore fluid from 0 to 15 weight percent reduces the energy of hydrate dissociation by almost 8 percent (Kamath and Godbole, 1987).

The essence of the hot-brine stimulation method, therefore, is the reduction in dissociation temperature that results from an increase in salinity. Reducing the dissociation temperature will decrease the thermal energy required to recover the chemical.

Documented Applicability and Limitations

The minimum reservoir porosity required for use of hot-brine injection is 15 percent. Below 15 percent porosity, gas production declines rapidly. Above 30 percent porosity, gas production does not change significantly. Hydrate dissociation energy is directly proportional to porosity, so excessive porosity--greater than about 50 percent--is also undesirable (Kamath and Godbole, 1987).

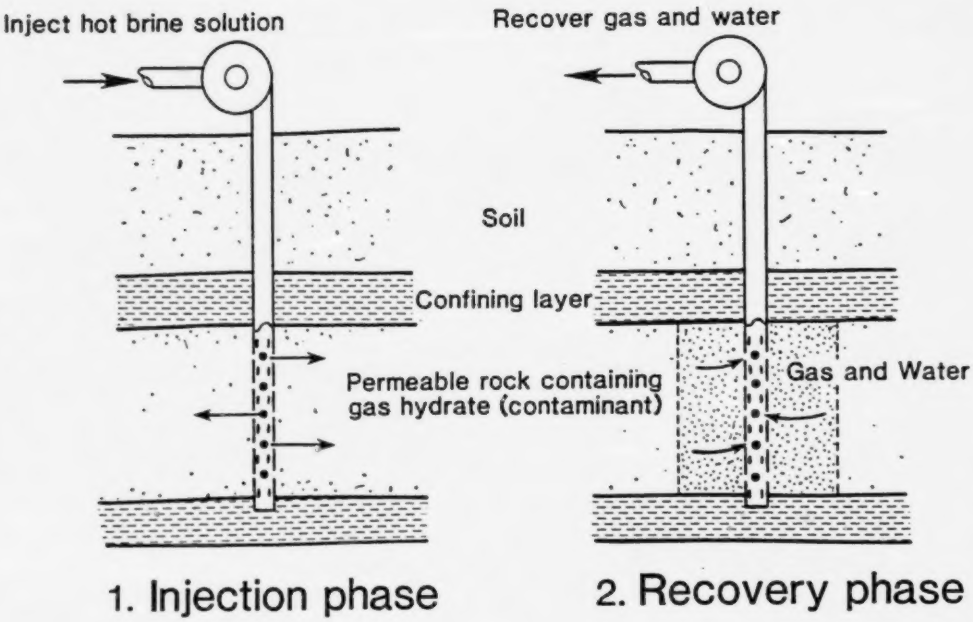
Inject hot brine solution
Recover gas and water
Soil
Confining layer
Permeable rock containing gas hydrate (contaminant)
Gas and Water
1. Injection phase
2. Recovery phase

Figure 11. Schematic diagrams showing the phases of hot-brine stimulation: (1) injection of hot brine into a zone of gas hydrate, followed by (2) recovery of dissociated gas and water (after Kamath and Godbole, 1987).

Thickness of the hydrate zone should be greater than 7 meters, to minimize heat loss to surrounding rock or earth, especially to overlying material. Energy efficiency of hot brine stimulated recovery increases significantly with increasing thickness of hydrate zone, up to a thickness of about 100 meters, beyond which the increased energy efficiency is small (Kamath and Godbole, 1987).

Quartz sand is less likely to respond to increased temperature and salinity than carbonate rocks or clay-rich soils. Salt precipitation may cause pore occlusion, which would hamper gas recovery, over extended periods of time.

Fractured rock is undesirable, because fractures will lead to rapid dissipation of heat.

Optimal brine temperatures are between 120^{o} and 200^{o}C. Very high brine temperatures result in severe heat loss and reduction in energy-efficiency ratio. Very low brine temperatures require high injection rates to achieve significant gas production (Kamath and Godbole, 1987).

According to theoretical analyses, the efficiency of gas production via hot-brine stimulation ranges from 150 to 200 m^3 of gas produced per m^3 of brine injected. The highest return of gas is for the highest salinity of brine.

The rate of gas production increases with the rate of brine injection. A 533 percent increase in brine injection rate results in a 267 percent increase in gas production rate, over a 3-year period.

The ratio of the heat value of gas produced versus heat injected, the energy efficiency ratio, varies from 5 to 11. It increases with porosity, reservoir layer thickness and burial depth, brine injection rate, salinity and temperature (Kamath and Godbole, 1987).

Status

Hot-brine injection is a *conceptual* technology potentially used for recovery in remedial applications. Hot-brine injection technology is not currently being investigated.

Hot-brine injection is a *conceptual* technology for general applications. Hot-brine injection technology is being investigated at the bench-scale for application in enhanced oil recovery. This research is being conducted at the University of Alaska. Principal investigators include V. A. Kamath and S. P. Godbole.

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IN SITU COMBUSTION

In situ combustion methods are used to recover highly viscous crude oil from tar sands and other deposits of viscous hydrocarbons (Kuhn and Koch, 1953). Similar techniques could possibly be used to recover hydrocarbons from uncontrolled hazardous waste sites.

Description

In situ combustion uses an injection and production well system to create and migrate a thermal front within an oil-bearing horizon. The thermal front advances from the injection well towards production wells at rates ranging from 1 to 36 inches/day (Gates and Ramey, 1958; Koch, 1965). As the front advances and the formation temperature increases, lighter oil fractions are mobilized through volatilization and reduced viscosity (Fig. 12).

The mobilized oil, formation water, and volatile components are transported ahead of the advancing combustion front. The heavier oil fractions are not mobilized but are broken down into coke which is consumed as fuel by the advancing thermal front. About 15 percent by weight of the initial oil in place is usually consumed (Gates and Ramey, 1985). Carbon dioxide and water are the primary by-products of combustion (Fig. 12).

The oil that is transported away from the combustion zone is concentrated in a constantly growing region of high oil saturation. The oil saturation results from the combined effects of gas, water, and steam drive and the volatilization of virgin oil (Lerner and others, 1985). Production wells recover mobilized oil and displaced volatile hydrocarbons, which condense in response to the decreasing thermal gradient away from the combustion front (Fig. 12).

Ignition is generally accomplished by preheating the reservoir with steam to temperatures on the order of 400°F and then pumping air down the injection well. The combination of air injection and increased formation temperature cause the oil adjacent to the injection well to oxidize and then ignite. The thermal front is maintained by continuously injecting air.

Documented Applications and Limitations

Controlled in situ combustion has been successfully employed to recover oil from depths as shallow as 100 feet. The method is relatively insensitive to permeability, with successful applications reported in low permeability reservoirs.

An early examination of in situ combustion was conducted on a 15 to 20 ft thick sand lens, located 180 ft below ground in southern Oklahoma (Kuhn and Koch, 1953). Precombustion oil production rates averaged 0.3 bbl/day. After the combustion front reached the extraction wells, production rates increased to approximately 1.45 bbl/day.

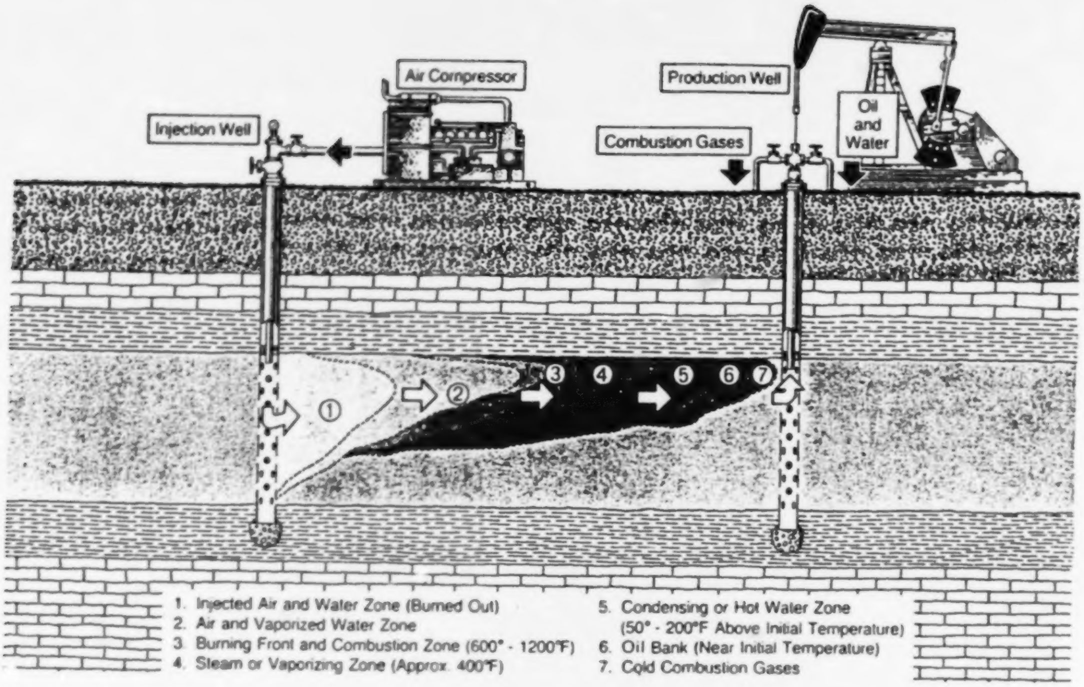
Air Compressor
Production Well
Injection Well
Combustion Gases
Oil and Water
①
②
③
④
⑤
⑥
⑦
1. Injected Air and Water Zone (Burned Out)
2. Air and Vaporized Water Zone
3. Burning Front and Combustion Zone (600° - 1200°F)
4. Steam or Vaporizing Zone (Approx. 400°F)
5. Condensing or Hot Water Zone (50° - 200°F Above Initial Temperature)
6. Oil Bank (Near Initial Temperature)
7. Cold Combustion Gases

Figure 12. Schematic of an in-situ combustion operation. A fire is ignited within the contaminated formation and is advanced toward a recovery well by the injection of air. Recovery is increased because some contaminants are vaporized, whereas the viscosity of other contaminants is reduced which facilitates their recovery as liquid phases (after Donaldson and others, 1985).

Gates and Ramey (1958) report that in situ combustion produced 51 percent of the oil in place compared with the expected rate of 10 percent to 15 percent using conventional methods at a 2.5 acre test tract of the Tulare oil sand, South Belridge field, Taft, California. The average rate of oil production during combustion was seven times greater than before combustion.

The first example of an extended combustion drive operation took place on a 1.75 acre test area at the West Newport field in Orange County, California. The reservoir is composed of highly unconsolidated and highly permeable sands ranging from fine to coarse grained with the productive interval located over 1000 ft below ground. In situ combustion was continued uninterrupted from 1958 to 1964, improving production by 50 percent, producing 500,000 bbl more of heavy crude oil than would be normally expected (Koch, 1965).

Moss and others (1959) found that average oil production rates increased four-fold during an in situ combustion test on the Pontotoc oil sand in southern Oklahoma. The sand averages 17 ft in thickness and 195 ft below ground surface. It was estimated that of the 1349 bbl produced during the test, 1043 were produced from the combustion drive.

More recently, White (1985) noted that combustion increased production in a reservoir from 6.1 percent of the original oil in place to 22.2 percent with ultimate recovery estimated to be 41 percent of the original oil in place.

It is important to note that these figures do not include the percent of original oil which is consumed by the combustion. Thus, the amount of oil actually removed from the reservoir is greater than the figures cited.

White (1985) reported that in situ combustion out-performs other enhanced oil recovery techniques in fine-grained reservoirs. The reason for this is that the high specific surface areas of fine-grained sediments enhance the formation and deposition of coke. An increase in the formation of coke increases the self-sustained burn, increases the volatilization and mobilization of lighter hydrocarbons, and produces carbon dioxide gas and steam which mobilize and drive the hydrocarbons.

Status

In situ combustion is a *conceptual* technology potentially used for recovery in remedial applications. In situ combustion technology is not currently being investigated.

In situ combustion is a*n developed* technology for general applications. In situ combustion technology has been tested by the petroleum industry to recover highly viscous hydrocarbons.

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RADIO-FREQUENCY HEATING

Radio-frequency (RF) heating is an in situ technique intended to recover volatile organic compounds by exposing contaminated soils to electromagnetic energy. Two general RF heating techniques to decontaminate soils have been investigated: thermal vaporization and recovery of contaminants with low boiling points, and the improvement of the reaction rate between the contaminants with high boiling temperatures and applied reagents (Dev and others, 1986).

Description

The RF heating technique was developed in the 1970's for thermal recovery of hydrocarbons. Most of these heating systems were designed for deposits of oil shale, tar sand, and other hydrocarbonaceous resources (Carlson and others, 1981). The same techniques developed for oil recovery have been investigated for application to hazardous waste site remediation.

Electromagnetic (EM) energy is applied to the contaminated soil through bound-wave exciter electrodes (Dev, 1986). The electrodes are either at the ground surface (fringing-field line) or emplaced in boreholes drilled into the site (triplate line; Dev and others, 1986). The bound-wave exciters send an EM wave into the contaminated soil when electromagnetic energy is supplied to the electrode network (Fig. 13).

The technique uses molecular agitation, rather than thermal conduction, to heat the soil (Dev and Downey, 1988). The agitation occurs through ohmic and dielectric mechanisms as the EM wave is attenuated. Ohmic heating occurs from resistance to ionic or conduction current flow, whereas dielectric heating results from the distortion of the atomic or molecular structure of polar materials in response to an alternating current (AC) generated by the EM wave. The AC field changes rapidly, and the alternating distortions dissipate mechanical energy, and translate it into thermal energy in the material (Dev, 1986).

The electromagnetic energy is applied in the RF band using a radio transmitter (Dev and Downey, 1988). Frequencies used to heat contaminated soil and rock vary from 2 and 45 megahertz. The choice of frequency is based upon the dielectric properties of the soil and the size of the area to be treated. Efficient in situ RF heating requires that EM radiation be fully contained within a defined volume of soil through the use of bound-wave EM exciters (Dev, 1986).

Temperatures generated using RF heating for decontamination generally exceed 150^{o}C, but locally they may reach 400^{o}C. A residence time of 1 to 2 weeks is required to heat the contaminated medium to these temperatures (Dev and others, 1984; Dev and Downey, 1988).

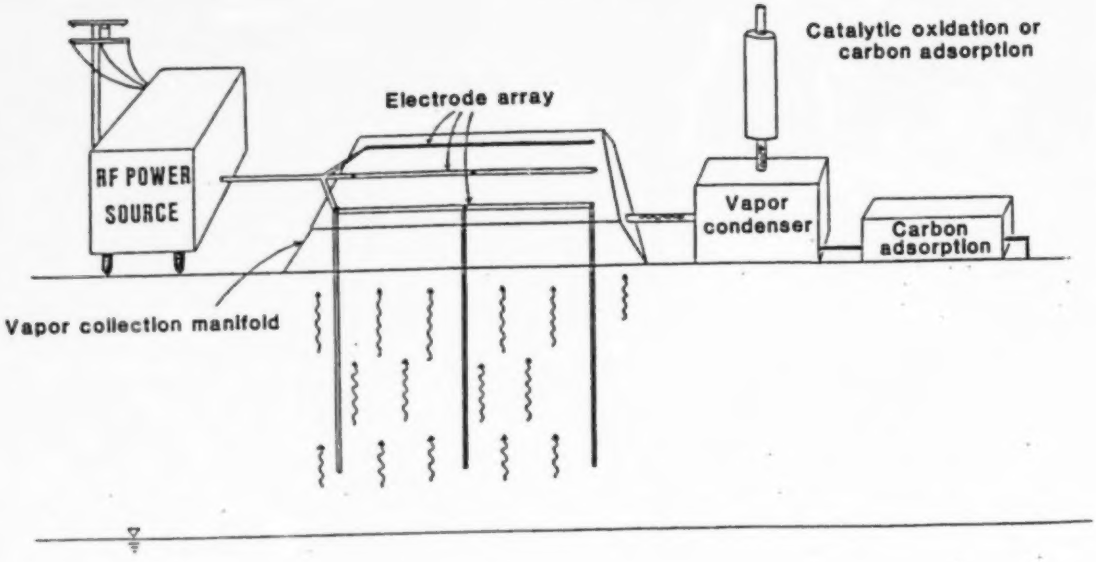
Catalytic oxidation or carbon adsorption
Electrode array
RF POWER SOURCE
Vapor condenser
Carbon adsorption
Vapor collection manifold

Figure 13. Schematic of a radio frequency heating operation. Electromagnetic energy is applied to a soil contaminated by volatile organics. Electrical resistance and distortion of the molecular structure of polar materials heat the soil (after Dev and Downey, 1988).

Documented Applications and Limitations

Preliminary investigations indicate that RF heating may be applied to almost any natural material in the subsurface. The amount and depth of heating due to RF sources depends on the dielectric properties of the medium and the wave properties of the applied EM energy. Thus, the volume and dielectric properties of a soil determine the frequency of optimal heating (Dev, 1986).

RF heating is most effective as a decontamination technique for volatile organic contaminants located above the water table. Using RF methods to heat the soil increases the volatilization of low-boiling point contaminants and thereby accelerates recovery. Other techniques, such as those described in the Vapor Extraction section (Section 10), would then be required to remove vapor from the subsurface.

RF heating can also be used to increase the reaction rate between contaminants and some types of treatment solutions. A chemical dechlorinating agent used in conjunction with RF heating can effectively dehalogenate certain contaminants, such as PCB's (Dev, 1986).

A bench-scale experiment using RF heating removed 95 percent of tetrachloroethylene from a contaminated soil column (AFESC/RDV, 1988).

RF heating was tested at the pilot- and field-scale at a fire training area of Volk Field Air National Guard Base, Wisconsin. Three rows of electrodes (13 per row) covering an area of 6 ft by 12 ft to a depth of 7 ft were installed in the training area. The field test ran for 11 days, raising soil temperatures to between 150^{O}C and 160^{O}C. Analysis indicates that the process removed 98.2 to 99.9 percent of the volatiles (low boiling point pollutants) and 68 to 99.9 percent of the semivolatiles (high boiling points pollutants) contaminating the site (Dev and Downey, 1988).

Status

Radio-frequency heating is a *developed* technology used for recovery in remedial applications. RF heating is being investigated at the bench-, pilot- and field-scale levels for the Air Force Installation Program. The principal investigator is Harsh Dev of the Illinois Institute of Technology's Research Institute (IITRI) in Chicago, Illinois.

Radio-frequency heating is a *developed* technology for general applications. RF heating has been tested at the bench-, pilot- and field-scale levels for application in enhanced oil recovery (Sresty and others, 1986). This research was conducted at IITRI with funding from the U.S. DOE and the U.S. EPA.

Sources

Data on radio-frequency heating technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Don Sanning, of the USEPA HWERL, Cincinnati, Ohio and Harsh Dev of IITRI, Chicago, Ill.

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CYCLIC PUMPING

Cyclic pumping is a delivery and recovery technique that systematically varies rates of either injection or extraction in an effort to minimize pumping costs. The optimization of pumping practices has the potential to reduce remediation costs at hazardous waste sites.

Description

In conventional pump and treat operations, the pumping rate is typically held constant. In a cyclic pumping operation, the rate is variable; pumps are turned on during an *active cycle* and turned off during a *rest cycle*. Cyclic pumping can be used for either the injection of treating solutions or the extraction of contaminated groundwater (Fig. 14; Keely and others, 1987).

A rest cycle allows time for diffusion between high-permeability pathways (fractures or large pores) and low-permeability blocks between them. Treating solutions diffuse from the pathways into the blocks, whereas contaminants diffuse from the blocks to the pathways during a rest cycle.

The active cycle of cyclic pumping is designed to deliver the minimum volume of nutrients or reactants, or remove the minimum volume of reaction products at the maximum possible concentration, or both (Keely and others, 1987).

Documented Applications and Limitations

Because there are no documented applications of cyclic pumping at remedial sites, there is no information on applicable site conditions. But it appears that cyclic pumping will be most effective in media composed of preferred flow paths and matrix blocks.

The petroleum industry uses cyclic techniques, including cyclic water flooding and steam stimulation (cyclic injection), for enhanced oil recovery. Cyclic water flooding consists of a period of water injection to restore reservoir pressure followed by an extended period of oil production. Once production drops off, water is again injected and the cycle repeated (Aguilera, 1980). Steam stimulation or cyclic injection uses a single well to inject steam and, after a "soaking" period, to recover the steam-mobilized oil (Latil and others, 1980).

The cyclic pumping technique is intended to increase the efficiency of pump-and-treat systems by increasing the concentration of contaminants recovered (or reactants delivered). The diffusion that occurs during the rest cycle between the matrix blocks and the pathways is the rate-limiting step during recovery (Fig. 14). In general, the rate of diffusion between matrix blocks and pathways will be slower during cyclic pumping than during steady pumping. As a result, it is expected that a decrease in the volume of recovered groundwater will be the principle advantage and a decrease in recovery rate will be the principle disadvantage of cyclic pumping.

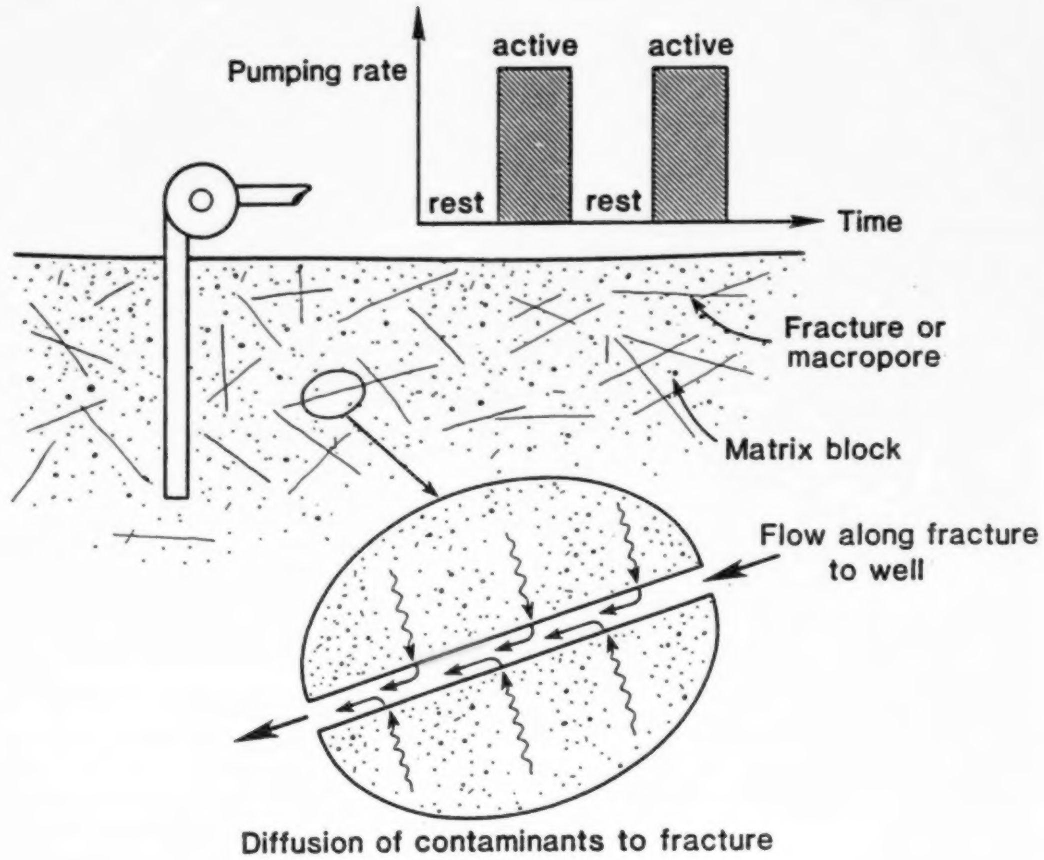
Pumping rate
active
active
rest
rest
Time
Fracture or macropore
Matrix block
Flow along fracture to well
Diffusion of contaminants to fracture

Figure 14. Processes involved in cyclic pumping. The rest period during a pumping cycle allows diffusion from the matrix to the fractures thereby increasing the contaminant concentration and decreasing the volume of recovered groundwater when compared with continuous pumping.

Status

Cyclic pumping is a *conceptual* technology that potentially can be used for both delivery and recovery in remedial applications.

Cyclic pumping is an *available* technology for general applications. Related cyclic pumping technologies are used by the petroleum industry for enhanced oil recovery.

Sources

Data on cyclic pumping technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Jon Herrmann, USEPA HWERL, Cincinnati, Ohio.

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SOIL FLUSHING

In situ soil flushing is done to accelerate the movement of a contaminant through unsaturated materials (Nash and Traver, 1986). A treatment solution is applied to the soil and allowed to percolate downward and interact with contaminating chemicals. Contaminants are mobilized by the treatment solution and transported downward to a saturated zone where they are pumped to the surface.

Description

The treatment solution can be delivered to the contaminated zone by using either gravity or forced methods. Forced delivery consists of various pumping techniques. Gravity delivery methods include surface flooding, ponding, spraying, ditching and subsurface infiltration beds and galleries (Fig. 15; EPA/540/2-86/002).

The efficacy of soil flushing is related to two processes: the increase in hydraulic conductivity that accompanies an increase in water content of unsaturated soil, and the engineering of treatment solutions to the composition of the contaminants and the contaminated medium.

The hydraulic conductivity of unsaturated soils decreases markedly with decreases in water content. As a result, flow of liquids through unsaturated soils is extremely slow and recovery of contaminants by conventional pumping techniques is impractical. Soil flushing overcomes this problem by increasing the water content and, therefore, increasing the hydraulic conductivity of the soil.

In many cases, pure water can be used to flush or mobilize water-soluble contaminants, but most innovations in soil flushing lie in the development of new treatment solutions. Surfactants can be added to increase the mobility of certain contaminants or chelating agents can be used to chemically react with and solubilize heavy metals. Acidic or alkaline solutions can be used to mobilize, neutralize, or destroy certain contaminants (Ellis and others, 1986; Dietz and others, 1986).

Surfactants promote the preferential wetting, solubilization or emulsification of certain types of organic contaminants by reducing the surface tension between two liquids or a liquid and a solid. Surfactants provide the link between the polar water molecule and nonpolar hydrophobic contaminants (Dietz and others, 1986).

Chelation is generally an equilibrium reaction between a metal ion and a complexing agent. In these complexes, a group of anions or molecules (ligands) surround the metal ions. Chelating agents (polydentate ligands) form more than one bond between the metal ion and a molecule of the complexing (chelating) agent. Chelation results in a stable complex that keeps metals in solution for subsequent transport and removal (Sanning and Lewis, 1987).

The use of acidic or alkaline solutions to remove metals and certain basic organics from contaminated soil has met with limited success (Dietz and others, 1986).

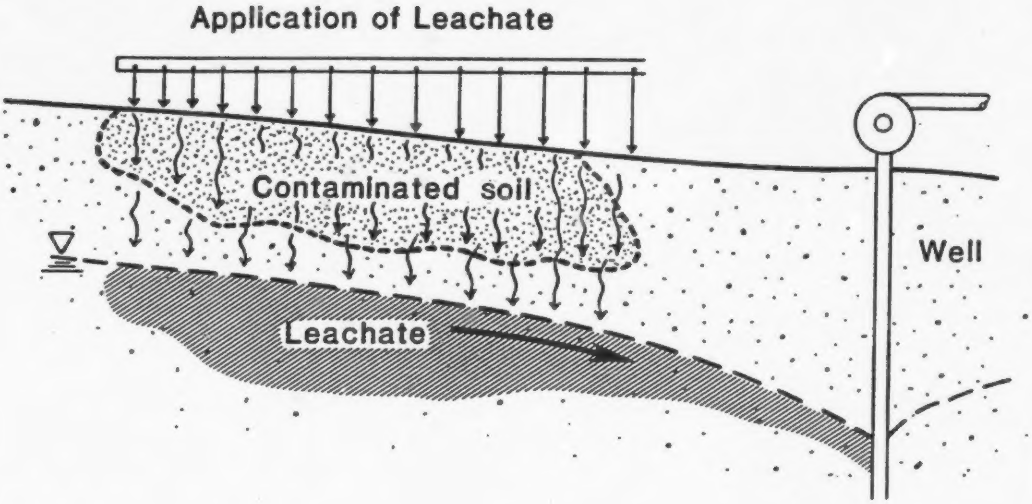
Application of Leachate
Contaminated soil
Leachate
Well

Figure 15. Schematic of a soil flushing operation. Flooding unsaturated soil mobilizes contaminants through dissolution and complexation. Contaminant migration to the water table is increased because of an increase in the hydraulic conductivity as the soil becomes saturated. Leachate is then recovered by pumping wells (EPA-540/2-84-003a).

Because of their inherent toxicity it is desirable to use low concentrations of these solutions (Sanning and Lewis, 1987). Acidic and alkaline solutions are used in cases of low volume but high contaminant concentration where the wastewater can be treated for safe disposal (Dietz and others, 1986).

Documented Applications and Limitations

Soil characteristics may affect the mobility of the contaminants during flushing. These include: grain size, specific gravity, density, and initial water content (Connick, 1986). Contaminated soils with saturated-hydraulic conductivities greater than 10^{-4} cm/sec are amenable to treatment with soil flushing (Nash and Traver, 1986). This excludes silt and clay soils (Davis and DeWiest, 1966).

Other limitations inherent to the soil flushing technique may restrict its application. Nonhomogeneities may cause channeling and uneven treatment of the contaminated medium (Ghassemi, 1988). Side reactions or sorption/retention of the treatment agent with the soil being flushed may make it impossible to limit reactions to the target contaminant and prevent the attenuation of the treatment agent (Ghassemi, 1988). Also, soil flushing may not be a viable technique for complex wastes composed of different contaminants with different solubilities (Ghassemi, 1988).

The amount of humic material in a soil also affects contaminant mobility by increasing the adsorption potential for organic contaminants. Soils with high concentrations of humic material and high contaminant levels may be excluded from treatment by soil flushing and require above ground treatment (Dietz and others, 1986). The cation exchange capacity of the soil may also affect contaminant removal by retarding the mobility of certain metals and metal salts.

Octanol/water coefficients can be used to estimate which organics can be mobilized by water flushing (Sanning and Lewis, 1987). Organics with octanol/water coefficients less than 1000 are considered water-mobile. These include the lower molecular weight alcohols and phenols, low to medium molecular weight ketones, aldehydes, and aromatics and the low molecular weight halogenated hydrocarbons (Sanning and Lewis, 1987).

The ability of soil flushing with surfactants to remove contaminants from model aquifers was first investigated for the American Petroleum Institute. These studies showed that soil flushing with surfactants can increase the solubility of gasoline in water (Texas Research Institute, 1985).

Removal efficiencies were greater than 90 percent for intermediate molecular weight aliphatic and aromatic hydrocarbons, polychlorinated biphenol mixtures, and chlorinated phenol mixtures in an early laboratory study of the effects of soil flushing with surfactants on soil contaminated with organic compounds (Ellis and others, 1983).

Subsequent studies indicated that sequential flushing of soil with three surfactants (ethylenediaminetetracetic acid, hydroxylamine hydrochloride, and citrate buffer) effectively removed metals from contaminated soil. Reported removal efficiencies were: 98 percent cadmium; 96 percent lead ; 73 percent copper; 52 percent chromium; and 23 percent nickel (Ellis and others, 1986).

Preliminary field tests on the efficacy of soil flushing were conducted at Volk Air National Guard Base, Camp Douglas, Wisconsin. Although the tests were statistically inconclusive, they did indicate that the soil flushing with surfactants did not realize expected contaminant removal rates (Nash and Traver, 1986).

A tetrachloroethylene spill in Sindelfingen, Land Baden-Wuerttemberg, West Germany, contaminated a 2,500 m^2 area of soil. Soil flushing was used to remediate the area, and after 18 months of operation contamination was reduced by 50 percent. Soil flushing continued for another 18 months and an additional 17 metric tons of contaminant were removed (Stief, 1984).

Recently, the EPA has developed a Mobile In situ Containment/Treatment System for use at hazardous waste sites (USEPA, 1982). This system can deliver specially prepared solutions of wash water into highly contaminated soil through 16 injectors. A vacuum applied to a series of wells draws the wash solution through the contaminated soil to the wells for removal and treatment at the surface. The system is capable of treating an area of contaminated soil up to 80,000 ft^2 in size (Traver, personal communication, 1988).

Status

Soil flushing is a *developed* technology used for recovery in remedial applications. Soil flushing technology is being investigated at the bench- and pilot- and field-scale levels. Developmental research is being monitored by the Releases Control Branch (RCB), Hazardous Waste Engineering Research Laboratory (HWERL), Edison, New Jersey.

Soil flushing (this technique is referred to as *soil washing* when used to remediate excavated soil) is an *available* technology for general applications. Soil washing is commonly used to treat excavated soils. This research is being monitored by the RCB, HWERL, Edison New Jersey.

Sources

Data on soil flushing technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Richard Traver, USEPA HWERL, Edison, New Jersey, who is project officer in charge of soil flushing research.

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GROUND FREEZING

Ground freezing has potential for remediation because contaminants apparently can be concentrated ahead of freezing fronts. By concentrating contaminants, artificial ground freezing can be used to reduce the volume of contaminated soil at a site and thereby facilitate remediation (Iskandar, 1986; Iskandar, 1987).

Description

In the late 1800's workers in the mining industry developed artificial ground freezing to sink shafts. The Poetsch method, developed in 1883, is still commonly used today (Iskandar, 1986). Basically, the ground is frozen by circulating coolant through steel casing installed in evenly spaced vertical boreholes (Fig. 16).

To implement the Poetsch method, a pipe approximately half the casing diameter is set inside each cased borehole. Coolant is circulated down the interior pipe returning along the outer casing. Usually brine is used as a coolant, but liquid nitrogen circulated in an open system can also be used. Liquid nitrogen has an advantage over brine because it can achieve a much lower temperature.

Almost any type of strata can be frozen (Harris and Pollard, 1986). Soil moisture content should exceed 11 percent by volume to achieve impermeability and a significant improvement in strength (Harris and Pollard, 1986).

Processes associated with the freezing of pore-water drive the migration of solutes. In frozen and freezing soil, water exists in three states: solid (ice), liquid, and vapor. When pore-water freezes slowly, crystals of nearly pure ice form, and any dissolved species are concentrated either in pockets or in thin films of liquid around solid particles (Iskandar, 1986). The water film around particles, in equilibrium with ice, can be very mobile in frozen soil allowing ion movement to occur (Iskandar, 1986).

Ion transport appears to occur through diffusion. Ions diffuse from zones of high concentration opposite the ice, through the free liquid phase in the soil pores, to lower concentration areas ahead of the freezing front.

The rate and extent of ion movement by this process depend on the concentration gradient of the ions in the soils, the rate of freezing, the water content and the types of ions in the soil (Iskandar, 1986) Complications arise from ion exchange and from the presence of ions that exist in more than one phase. The changing temperature and chemistry of the soil solution may cause chemical reactions that retard ion migration (Iskandar, 1986).

Documented Applications and Limitations

For remedial applications, artificial ground freezing was initially investigated as a technique to construct temporary barriers around hazardous waste spills and releases

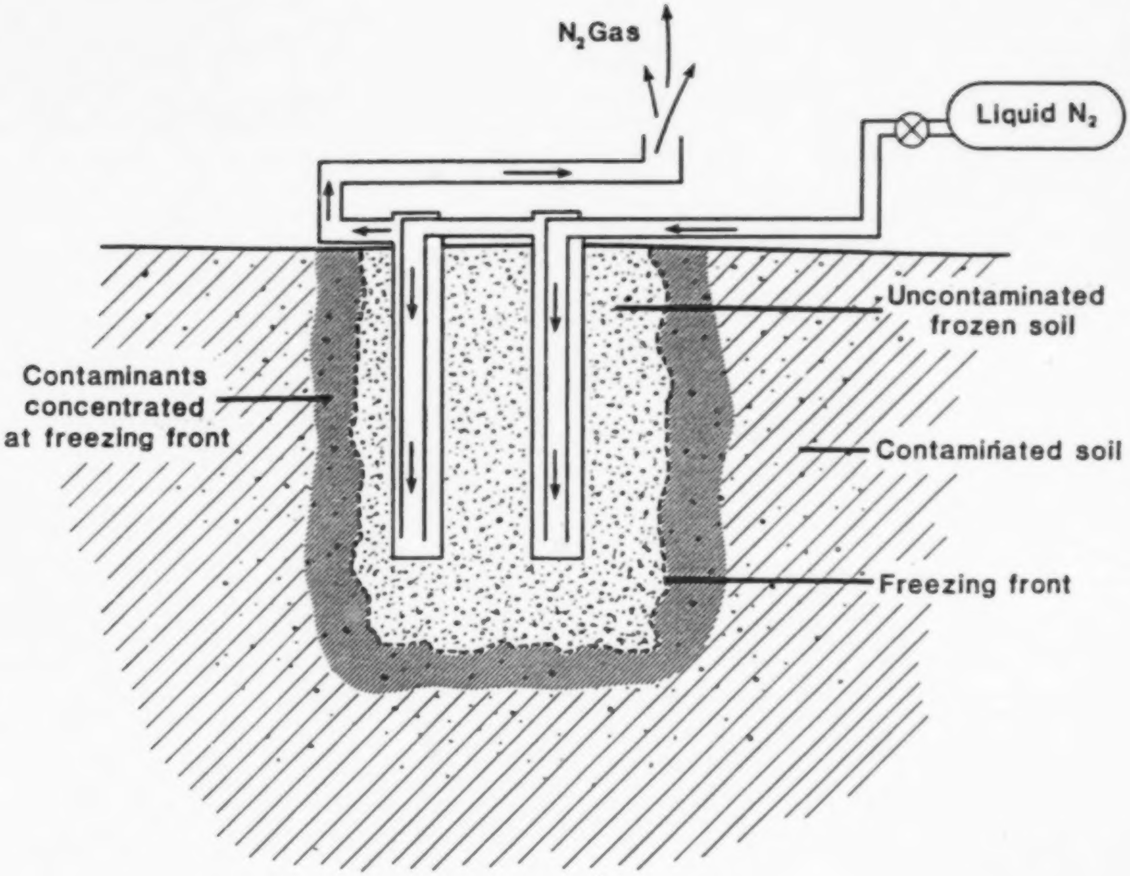
N_2 Gas
Liquid N_2
Uncontaminated frozen soil
Contaminants concentrated at freezing front
Contaminated soil
Freezing front

Figure 16. Processes involved in ground freezing. Liquid nitrogen is circulated through pipes in the subsurface initiating ground freezing. Contaminants are concentrated at and migrate ahead of the advancing freezing front. By concentrating the contaminants, the volume of soil that must be treated is reduced (after Sullivan and others, 1984).

(Fig. 16). These investigations indicated that artificial ground freezing may work best in saturated, coarse-grained soils and may not be as effective in fine-grained soils where moisture retention is typically high (Sullivan and others, 1984).

Research at the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) has shown that certain organic contaminants can be migrated and, concentrated and/or, volatilized when a contaminated soil is slowly frozen; contaminants that migrate during freezing are concentrated in a zone around the freezing front; and the concentration of certain inorganic compounds is reduced during freezing (Ayorinde and others, 1988).

The effects of various parameters such as freezing rate, soil types and density, and contaminant types and concentrations on the migration of contaminants in freezing soils have been evaluated. Freezing rate was found to be the most significant (Ayorinde and others, 1988).

Successful migration by freezing front growth has, so far, been limited to these volatile organic compounds: chloroform, benzene, and toluene and to these nonvolatile organic compounds: trinitrotoluene (TNT) and hexahydrotrinitrotriazine (HMX), according to Ayorinde and others (1988).

Preliminary results from soil column experiments indicate that artificial ground freezing can mobilize contaminants and reduced their concentration in soil columns subjected to partial freezing as compared with unfrozen soil columns. Reductions in the concentration of volatile organic compounds in the partially frozen columns ranged from 25 to 67 percent and reductions of nonvolatile organic compounds ranged from 2 to 38 percent (Ayorinde and others, 1988). Increases in contaminant concentration were noted in the vicinity of the freezing front.

Earlier tests results on the effect of freezing on contaminant mobility indicated that the concentration of nickel in leachate from a soil column subjected to a cycle of freezing and thawing increased substantially when compared with leachate from unfrozen soil. Concentrations of copper, cadmium, and zinc in the leachate from the frozen soil were only very slightly increased when compared with leachate from unfrozen soil (Iskandar and Jenkins, 1985).

Freezing and thawing cycles had the opposite effect on the concentration of organic contaminants in the leachate, decreasing the amount of contaminant leaching out of the soil. The reduction of volatile concentration in the leachate after the cycles was as high as 90 percent for chloroform, benzene, and toluene and as low as 45 percent for tetrachloroethylene with the reduction attributed to freezing-induced volatilization (Iskandar and Jenkins, 1985).

Recent research at CRREL has included the design and construction of a large-scale, prototype testing facility to study the transport of contaminants in soils during freezing (Ayorinde and others, 1988). A large-scale testing program is currently underway involving several types of volatile and non-volatile organic compounds (Ayorinde, 1988).

Status

Ground freezing is a *developed* technology used for recovery in remedial applications. Ground freezing technology is being investigated at the pilot- and field-scale levels at the US Army Corps of Engineers Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire. Principal investigators include Iskandar K. Iskandar and Femi Ayorinde.

Ground freezing is an *available* technology for general applications. Ground freezing technology is routinely used in civil engineering to increase rock and soil stability, desalinate seawater, and occasionally to treat industrial and sewage sludge.

Sources

Data on ground freezing technology were obtained primarily from the references listed in the following bibliography. Additional information was acquired by contacting Iskandar K. Iskandar and Femi Ayorinde of CRREL, who are currently researching ground freezing; and Doug Keller, USEPA HWERL, Cincinnati, Ohio, who is project officer in charge of ground freezing research.

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SECTION 3

SUMMARY

Innovative technologies of delivery and recovery offer a range of potentially valuable new methods of remediating contaminated sites. Further investigations that would develop the appropriate technologies to a level of routine field application should certainly reduce the risk of groundwater contamination.

To condense the descriptions in section 2 and to facilitate comparison of the different innovative technologies, the essential details are summarized here in table forms.

GENERAL CAPABILITIES AND PROCESSES

The general capabilities and processes of each technology are summarized in Table 1. The general capabilities include which phases--solid, liquid, or vapor--a particular technology is intended to either deliver or recover. The processes reveal some resemblances between the technologies, and they could serve as a preliminary basis for evaluating combinations of technologies at the same waste site.

The delivery of solid phases, either by hydraulic fracturing, radial drilling, or kerfing, could be done by injecting solid particles mixed with water either as a slurry or a colloidal suspension. The efficiency of delivering either liquid or vapor could be increased by cyclically varying the rate of injection. Colloidal gas aphrons offer a method of increasing the concentration of vapor that can be delivered, when compared with concentrations of the vapor dissolved in water.

Recovery of contaminants that occur as a liquid or a vapor can be increased by methods that increase the effective hydraulic conductivity (K_e) of the contaminated zone (e.g. hydraulic fracturing, radial drilling, ultrasonic methods, kerfing, and electro-kinetics). Those methods typically increase K_e by creating local zones of high permeability, such as sand-filled columns or layers. Ultrasonic methods are intended to increase permeability in the vicinity of a borehole. Electro-kinetics increases recovery because in tight soils the conductivity associated with flow driven by electric potential can be greater than that driven by hydraulic potential.

Jet slurrying is a unique method of recovery because it will allow any phase--solid, liquid or vapor--to be recovered. Jet slurrying is the only method reviewed that can be used to recover solid materials from the subsurface.

TABLE 1. SUMMARY DIAGRAM SHOWING THE PHASES THAT COULD BE EITHER DELIVERED OR RECOVERED BY THE PARTICULAR INNOVATIVE TECHNOLOGIES AND THE BASIC PROCESSES USED IN THE TECHNOLOGY

	TECHNOLOGY	Delivery	Recovery	Comment
1.	Colloidal gas aphrons	--V*	---	Deliver vapor at high conc.
2.	Hydraulic fracturing	SLV	-LV	Increase K_e of formation
3.	Radial drilling	SLV	-LV	Increase K_e of formation
4.	Ultrasonic methods	---	-LV	Increase K_e near well bore
5.	Kerfing	SLV	SLV	Increase K_e of formation
6.	Electro-kinetics	-L-	-L-	Increase K_e of tight soils
7.	Jet slurrying	---	SLV	Remove soil and contaminant
8.	CO_2 injection	---	-L-	Decrease visc. of contaminant
9.	Polymer injection	---	-L-	Increase visc. of water
10.	Vapor extraction	---	-LV	Increase cont. vaporization
11.	Steam stripping	---	-LV	Increase vapor., decrease visc.
12.	Hot brine injection	---	-LV	Increase vapor., decrease visc.
13.	In situ combustion	---	-LV	Increase vapor., decrease visc.
14.	Radio frequency heating	---	-LV	Increase vapor., decrease visc.
15.	Cyclic pumping	-LV	-LV	Increase conc., decrease volume
16.	Soil flushing	---	-LV	Increase cont. solubility
17.	Ground freezing	---	-L-	Diffusion due to phase exclusion

* possible phases for delivery or recovery are S(solid), L(liquid), and V(vapor)

K_e refers to hydraulic conductivity

Several methods are designed to decrease recovery costs by increasing the concentration and decreasing the volume ofcontaminated groundwater. For example, when compared with conventional pumping at a constant rate, cyclically varying the rate of pumping at recovery wells could reduce the volume and increase the concentration of contaminants. Methods of soil flushing are designed to increase the concentration of contaminants in recovered groundwater by using one of a variety of chemical methods of increasing solubility. Ground freezing is intended to increase the concentration of liquid contaminants because the contaminants are excluded from liquid water during the phase change of water to ice.

Methods that could aid the recovery of liquids either by reducing their viscosity or by increasing the viscosity of water include polymer injection, CO_2 injection, and such thermal methods as steam stripping, hot brine injection, in situ combustion, and RF heating. Thermal methods are also applicable to the recovery of vapor phases or to liquids with relatively low latent heat of vaporization.

SITE CONDITIONS

Most technologies are effective for delivery or recovery under certain site conditions, and their effectiveness may be limited or negligible under other conditions. Thus, the development of some technologies could be encouraged because they offer application over a broad range of conditions, whereas the development of other technologies could be warranted because they could be effectively applied to a single but particularly dangerous condition.

Site conditions are used in this report to describe the factors related to contaminant chemistry, local geology (including soil type), and local hydrology that affect transport processes related to delivery or recovery. Because a complete list of these factors would be too long and of little use, an abridged list describing site conditions specifically tailored to fit the needs of this summary of innovative technologies was developed (Table 2). First, a complete list of all possible factors was made. Then those factors that were not specifically addressed by any technology were eliminated because they gave no additional insight into the relative conditions of applicability of the technologies. For example, adsorption of some chemicals onto some types of mineral grains will reduce the rate of recovery of the contaminant. We excluded adsorption as a site condition, however, because we could find no data suggesting that any of the technologies were particularly well-suited to reducing the effects of adsorption.

Factors related to the chemistry of contaminants included as site conditions are: miscibility in water, density, and vapor pressure. In particular, the density of the contaminant is compared with that of water so that the location with respect to the phreatic surface can be inferred. Furthermore, the vapor pressure is considered only qualitatively to determine whether the contaminant could be driven into a vapor phase in unsaturated media.

Factors related to local hydrology include the degree of saturation of the contaminated zone. This provides a fundamental distinction between processes involving flow of liquids and flows of vapors, because it is assumed that extremely low liquid hydraulic conductivity essentially precludes flow of liquid in unsaturated material.

TABLE 2. SUMMARY DIAGRAM OF THE SITE CONDITIONS NEEDED TO APPLY THE VARIOUS TECHNOLOGIES TO REMEDIAL ACTIONS

	a. UNSATURATED		SATURATED					
	b.		c. IMMISCIBLE		MISCIBLE			
			d.		e. UNIFORM K		NONUNIFORM K	
					f.		g.	
	VOLATILE	NONVOLATILE	$P \leq H_2O$	$P > H_2O$	HIGH K_e	LOW K_e	PREFERRED FLOWPATH	HETERO-GENEOUS
1. Colloidal gas aphrons	–*	–	E	E	–	–	e	e
2. Hydraulic fracturing	E	E	E	E	E	–	e	e
3. Radial drilling	E	E	E	E	E	e	E	e
4. Ultrasonic methods	–	–	C	C	C	C	C	C
5. Kerfing	e	e	e	e	e	e	e	e
6. Electro-kinetics	–	–	–	–	D	–	–	–
7. Jet slurrying	C	C	C	C	C	C	C	C
8. CO_2 injection	–	–	C	C	–	–	–	–
9. Polymer injection	–	–	C	C	–	–	C	C
10. Vapor extraction	D	–	–	–	–	–	–	–
11. Steam stripping	D	d	D	D	–	–	–	–
12. Hot brine injection	C	–	c	–	–	–	–	–
13. In situ combustion	C	c	C	–	–	–	–	–
14. Radio frequency heating	D	–	–	–	–	–	–	–
15. Cyclic pumping	C	–	C	C	–	–	C	–
16. Soil flushing	D	D	–	–	–	–	–	–
17. Ground freezing	d	–	–	–	d	D	D	D

*

D, d:	Developed	Uppercase: Inferred to be applicable
E, e:	Emerging	Lowercase: Inferred limited applicability
C, c:	Conceptual	Dash: Inferred to be inapplicable

Factors related to the local geology affect the hydraulic conductivity, K_e, of the contaminated medium. Materials of uniformly distributed hydraulic conductivities are subdivided into materials of relatively low ($< 10^{-6}$ cm/sec) or relatively high conductivity ($> 10^{-6}$ cm/sec). Because the hydraulic conductivity of many natural materials is nonuniformly distributed, and two types of nonuniform distribution are considered: preferred flowpaths and heterogeneous materials, which differ in the scale of the nonuniformity. Preferred flowpaths are fractures or macropores that separate matrix blocks of much lower permeability. Heterogeneous materials are characterized by lenses or layers of contrasting permeability. Typically, heterogeneities are much larger than preferred flowpaths.

The various factors describing site conditions can be conveniently assembled in a decision tree (located at the top of Tables 2 and 3). The tree is based on the following questions:

a. Is the site saturated?
b. Is the contaminant volatile?
c. Is the contaminant miscible in water?
d. Is the density of the contaminant greater than water?
e. Is the hydraulic conductivity distributed uniformly?
f. Is the hydraulic conductivity low?
g. Are there preferred flowpaths, or heterogeneities?

The four possible states of development for each technology are based on developmental states used elsewhere by the EPA:

1. Available: Technology is fully proven and available for use.

2. Developed: Technology has passed bench and pilot-scale testing, but lacks thorough field testing.

3. Emerging: Research in progress, bench and pilot-scale testing incomplete.

4. Conceptual: Technology appears to be applicable to remediation, but research has yet to be initiated.

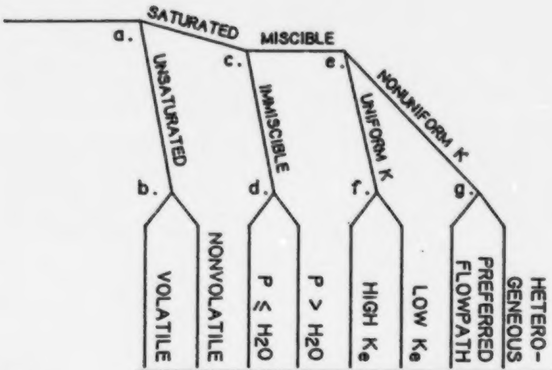
The level of effectiveness of each technology is evaluated for each of the site conditions:

1. Effective (applicable)
2. Limited effectiveness (limited applicability)
3. Not effective (inapplicable)

Levels of effectiveness under the various site conditions are inferred from results of conceptual analysis, bench- or pilot-scale experiments, preliminary field tests, or analogies to applications in related fields. Thus, the data summarized in Tables 2 and 3 reflect *our judgment* based on preliminary findings rather than the results of field testing under actual site conditions.

Many of the innovative technologies have been developed for applications other than remedial action. The level of effectiveness is typically better documented and the

TABLE 3. SUMMARY DIAGRAM OF THE SITE CONDITIONS NEEDED TO APPLY THE VARIOUS TECHNOLOGIES TO GENERAL APPLICATIONS



	VOLATILE	NONVOLATILE	$P \leq H_2O$	$P > H_2O$	HIGH K_e	LOW K_e	PREFERRED FLOWPATH	HETEROGENEOUS
1. Colloidal gas aphrons	–*	–	D	D	E	e	e	e
2. Hydraulic fracturing	E	E	E	A	A	–	a	a
3. Radial drilling	E	E	E	D	D	d	D	e
4. Ultrasonic methods	–	–	C	A	C	A	C	C
5. Kerfing	A	A	A	A	A	A	A	A
6. Electro-kinetics	–	–	–	–	A	A	–	–
7. Jet slurrying	D	D	D	D	D	D	D	D
8. CO_2 Injection	–	–	C	A	–	–	–	–
9. Polymer Injection	–	–	C	A	–	–	C	C
10. Vapor extraction	A	–	–	–	–	–	–	–
11. Steam stripping	A	a	A	A	–	–	–	–
12. Hot brine injection	C	–	c	–	–	–	–	–
13. In situ combustion	D	–	D	d	–	–	–	–
14. Radio frequency heating	D	D	–	–	–	–	–	–
15. Cyclic pumping	C	–	C	A	–	–	c	–
16. Soil flushing	A	A	–	–	–	–	–	–
17. Ground freezing	a	–	–	–	a	A	A	A

*A, a: Available
D, d: Developed
E, e: Emerging
C, c: Conceptual

Uppercase: Inferred to be applicable
Lowercase: Inferred limited applicability
Dash: Inferred to be inapplicable

state of development is commonly much greater than they are for remedial applications. A summary of the level of effectiveness at various site conditions for any application, including remedial actions, is shown in Table 3.

STATE OF DEVELOPMENT

The general state of development of a particular technology is related to how quickly that technology can be made field-ready for remedial action. The state of development of each technology for both remedial and general applications are summarized in Table 4. Data shown in Table 4 can also be obtained from Tables 2 and 3.

Most innovative delivery or recovery technologies are used routinely for applications other than remedial actions. For example, the mining industry uses colloidal gas aphrons to separate clay particles during the preliminary washing of phosphate ores.

Hydraulic fracturing is used extensively within the petroleum industry both to increase the recovery of hydrocarbons from low permeability reservoirs and to enhance the delivery of fluids used to displace petroleum in sweeping operations. Horizontal radial drilling is a technique similar to hydrofracturing in that it was originally developed for use in the petroleum industry both to increase the recovery of oil and to enhance the delivery of fluids to oil-bearing formations. Applications of radial drilling to petroleum recovery have been limited to bench and pilot-scale testing, reflecting the relative infancy of the technology.

Ultrasonic methods are used by soil scientists to disperse very fine particles and remove clay aggregates and mineral films coating sand grains. Ultrasonic cleaners are used in a wide range of industrial cleaning procedures and high intensity ultrasonic probes are available that disintegrate cells for microbiological examination. We are unaware of any previous application of ultrasonic techniques to reduce low permeability skins on wells.

Kerfing is commonly used in the petroleum industry to notch boreholes. A technique similar to kerfing, jet grouting, is used for a variety of geotechnical applications. Jet grouting is currently being investigated by the research branch of Halliburton Services Company at Duncan, Oklahoma.

The application of an electric field to an unstable soil is a proven and frequently used construction technique to dewater and stabilize soil. Electro-kinetics has been used since the 1930's in this capacity.

Jet-induced slurry mining is used to remove ore bodies at depth without the removal of overburden. The U.S. Bureau of Mines has investigated this technology and has developed a state-of-the-art borehole mining tool.

Carbon dioxide flooding injects CO_2 into an oil-bearing formation for the purposes of maintaining reservoir pressure and reducing the viscosity of the oil. CO_2 injection is a commonly used enhanced oil recovery technique. Polymer flooding is another enhanced oil recovery technique, relying on water-soluble polymers either to increase the viscosity of the flooding fluid and thereby decrease the viscosity contrast between

TABLE 4. SUMMARY OF THE DEVELOPMENT STATUS OF INNOVATIVE DELIVERY AND RECOVERY TECHNOLOGIES

		Application			
		Delivery		Recovery	
	TECHNOLOGY	General	Remedial	General	Remedial
1.	Colloidal gas aphrons	E*	E	A	NA
2.	Hydraulic fracturing	E	E	A	E
3.	Radial drilling	E	E	D	D
4.	Ultrasonic methods	NA	NA	A	C
5.	Kerfing	E	E	A	E
6.	Electro-kinetics	D	D	A	D
7.	Jet slurrying	NA	NA	A	C
8.	CO_2 injection	NA	NA	A	C
9.	Polymer injection	NA	NA	A	C
10.	Vapor extraction	NA	NA	A	D
11.	Steam stripping	NA	NA	A	D
12.	Hot brine injection	NA	NA	C	C
13.	In situ combustion	NA	NA	A	C
14.	Radio frequency heating	NA	NA	D	D
15.	Cyclic pumping	C	C	A	C
16.	Soil flushing	NA	NA	A	D
17.	Ground freezing	NA	NA	A	D

* Level of Development
A, available, fully proven and in routine use;
D, developed, passed bench- and pilot-scale testing;
E, emerging, research in progress,
C, conceptual, applicable but unevaluated;
NA, not applicable.

the oil and the driving fluid, or to form viscous gels in situ and homogenize reservoir permeability. Oil field service companies, such as Halliburton Services or Dowell Schlumberger, can perform either carbon dioxide or polymer injection. Vapor extraction techniques are used by the solid waste industry to control, treat, and recover methane generated at landfills. Methane extraction techniques have been used for several decades.

The steam stripping of hydrocarbons from coal beds, tar sands and asphalt deposits is employed by the petroleum and mining industries. Presently, 75 percent of all enhanced oil recovery operations use some form of steam stripping.

Hot brine injection is a recently conceived, but untested, enhanced recovery technique for natural gas. Theoretically, hot brine could be used to drive any natural gas occurring as a solid or liquid in the reservoir to the vapor phase for an easier recovery.

The use of in situ combustion techniques for the recovering of highly viscous hydrocarbons was investigated in the 1940's and 1950's. Recently the petroleum industry has shown a renewed interest in in situ combustion techniques.

Radio frequency (RF) heating was originally developed to recover hydrocarbons from oil shale and tar sands. The development of RF heating as a hydrocarbon recovery technique was taken to bench and pilot-scale by several investigators.

Cyclic pumping is an unevaluated delivery and recovery technique that systematically varies rates of either injection or extraction in an effort to minimize pumping costs. The petroleum industry uses related cyclic techniques for enhanced oil recovery. These techniques include cyclic waterflooding and steam stimulation (cyclic injection).

Soil washing is routinely applied to excavated soils. Numerous mobile soil containment/treatment units are commercially available for use on excavated soils.

Ground freezing has seen several applications by civil engineers. It was originally used to increase rock stability during the sinking of mine shafts and is currently being used to treat municipal wastewater, desalinate seawater, and treat industrial and sewage sludge.

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